ОБЩЕСТВО НА ТРИБОЛОЗИТЕ В БЪЛГАРИЯ

SOCIETY OF BULGARIAN TRIBOLOGISTS

ТРИБОЛОГИЧЕН ЖУРНАЛ БУЛТРИБ

TRIBOLOGICAL JOURNAL BULTRIB

Година VII, брой 07 (07), 2018
Volume VII, Number 07 (07) 2018

Доклади от 13-та международната конференция по трибология

BULTRIB'18, 25-27 октомври 2018, София, България

Papers from the 13th International Conference on Tribology

***BULTRIB'18**, 25-27 October 2018, Sofia, Bulgaria*

Printing House of the Technical University
Sofia

Трибологичен журнал БУЛТРИБ
Tribological Journal BULTRIB

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Sofia, 2018

ISSN: 1313-9878

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ОБЩЕСТВОТО НА ТРИБОЛОЗИТЕ В БЪЛГАРИЯ

със съдействието на
ФИТ на ТЕХНИЧЕСКИЯ УНИВЕРСИТЕТ - София

THE SOCIETY OF BULGARIAN TRIBOLOGISTS

with the assistance of the
FACULTY OF INDUSTRIAL TECHNOLOGY at the TECHNICAL UNIVERSITY OF SOFIA

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БАЛКАНСКА ТРИБОЛОГИЧНА АСОЦИАЦИЯ

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Tribologie & Hochtechnologie GmbH, Germany

Venue:

13th International Conference on Tribology ***BULTRIB '18****, 25-27 October 2018, Sofia,*
The Faculty of Industrial Technology at the Technical University of Sofia,
Block 3, Room 3201
Studentski Grad (Students'Town), Darvenitza, Sofia, Bulgaria

Topics:

• Contact Interaction, Friction and Wear.
Synergy in Tribology •
• Tribomechanics, Tribomaterials & Coating •
• Tribochemistry, Mechanochemistry •
• Lubrication & Lubricants •
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• Teaching Tribology •
• Interdisciplinary Nature of Tribology •

Hosts:

The Technical University of Sofia is the largest educational and scientific complex in Bulgaria in the field of technical and applied sciences with an institutional accreditation grade of 9.5 (on the scale of 10) for the period 2012 – 2018.

The Faculty of Industrial Technology (FIT) prepares specialists in the field of engineering and technology. Ever since the first academic year in 1945/1946 the Faculty has trained thousands of engineers and has always been a leading national center in the field of scientific research and applied activities. One of the Laboratories in FIT is the **Scientific & Production Laboratory "Tribology".**

Scientific and Production Laboratory "Tribology" – 44 years National Tribology Centre

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The scientific and production **Laboratory "Tribology"** is headed by Prof. Dr Mara Kandeva. The **Laboratory "Tribology"** was founded at the **Technical University Sofia** in 1974 by **Prof. DSc Nyagol Manolov**, and acts as National Tribology Centre in Bulgaria. It is the starting place for feeding the National WEB in the tribospace, which is a contact network of researchers/educators, customers and producers, and their achievements in the field of tribology and tribotechnologies. In sight are problems related to the management of friction, wear, lubrication, hermeticity, serviceability and reliability of tribotechnical elements and systems in their operation and maintenance. Lubricants, additives and surface coatings are the thoroughly developed topics of the latest years.

The latest tribotechnologies developed in the Laboratory "Tribology" at the Technical University – Sofia are **tribotechnologies for application of wear-resistant gas-flame and ultrasonic powder coatings** in collaboration with the Belgian company "GMA-Technologies. Another tribotechnology actual for Bulgaria and the region is a **tribotechnology for qualification and regeneration of air filters in motorcar and truck transportation**. The method and technology are patent of the Laboratory "Tribology", Sofia.

The Laboratory for Tribology, with the support of the Society of Bulgarian Tribologists, organizes the International Conferences on Tribology BULTRIB.

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ПРИВЕТСТВЕНО СЛОВО

проф. д-р Мара КАНДЕВА

Уважаеми г-н Зам. Ректор по науката,
Уважаеми г-н Декан,
Уважаеми проф. Манолов,
Скъпи колеги, гости и приятели,

С голямо удоволствие Ви приветствам с „Добре дошли“ на поредната 13-та конференция БУЛТРИБ'2018!

Изпитвам дълбоко удовлетворение и радост, че нашето трибологично семейство на Балканите вече 25 години провежда редовно своите срещи на трибологичните конференции в различните страни на Балканската трибологична асоциация – България, Гърция, Румъния, Сърбия и Турция. На тези конференции ние трибolозите споделяме своите постижения, трудности, нови идеи, печелим нови приятели и едновременно с това получаваме по-силна убеденост в неразкритите възможности на трибологията за човешкия просперитет.

Трибологията като интердисциплинарна наука и технология е органически свързана с глобалните проблеми на съвременната цивилизация – опазването на околната среда и енергийната ефективност и функционалност на индустрията.

Трибологичните процеси присъстват във всички етапи от жизнения цикъл както на природата и обществото, така и на технологиите и техниката при проектирането, изработването, експлоатацията и ликвидацията на съоръженията, механизмите и машините. Знанията за триенето, износването, смазването и контактната проводимост, постиженията на науката за материалите, нанотехнологиите, виртуалното инженерство, позволяват постигане на висока функционална и екологична надеждност на техническите съоръжения. Разработването на нови конструкционни и смазочни материали на основата на възобновяеми източници на енергия е от особено значение за грижата ни за Планетата, Обществото и Човека.

Вярвам, че дискусиите по тези въпроси на настоящата конференция ще родят нови идеи, ще провокират нашата креативност и мотивация за постигане на нови успехи в полза на човечеството.

Тук е мястото от името на българските триболози да изкажа своята благодарност на ръководството на Техническия университет-София в лицето на проф. д-р инж. Иван Кралов и на Машинно-техологичния факултет в лицето на проф. д-р инж. Георги Тодоров за доверието, моралната и финансова подкрепа, която оказват за развитието на трибологията.

Изказвам специална благодарност на проф. дтн Нягол Манолов – нашия учител и основател на българската и балканската трибология, за неговата креативност, дълбока мотивация и всеотдайност към идеите и последователите на трибологията.

Пожелавам на всички вас вълнуваща и ползотворна конференция!

Проф. д-р инж. Мара Кандева,
Председател на Обществото на триболозите в България,
Ръководител на Лаборатория „Трибология“,
Машинно-технологичен факултет
Технически университет – София

OPENING SPEECH

Prof. Dr Mara KANDEVA

Dear Mr. Vice Rector of Science,
Dear Mr. Dean,
Dear Prof. Manolov,
Dear colleagues, guests and friends,

It is my great pleasure to welcome you to the 13th BULTRIB'2018 Conference!

I am deeply pleased that our tribological family in the Balkans has been holding regular meetings at the tribological conferences in the different countries of the Balkan Tribological Association for 25 years now - Bulgaria, Greece, Romania, Serbia and Turkey. At these conferences we tribologists share our achievements, difficulties, new ideas, make new friends, and at the same time gain greater conviction in the undiscovered possibilities of tribology for human prosperity.

Tribology as an interdisciplinary science and technology is organically linked to the global problems of modern civilization - the protection of the environment and the energy efficiency and functionality of industry.

Tribological processes are present in all stages of the life cycle of both nature and society, as well as of technology and technics in the design, manufacture, operation and removal of facilities, mechanisms and machines. The knowledge of friction, wear, lubrication and contact conductivity, the achievements of material science, nanotechnology, and virtual engineering, make it possible to achieve high functional and environmental reliability of technical and natural facilities. The development of new construction and lubrication materials related to renewable energy sources is of particular importance to our concern for the Planet, Society and Man.

I believe that discussions on these issues at the present conference will give birth to new ideas, provoke our creativity and motivation to achieve new success for the benefit of humanity.

On behalf of the Bulgarian tribologists, I express my gratitude to the management of the Technical University-Sofia in the person of Prof. Dr. Eng. Ivan Kralov and of the Faculty of Industrial Technology in the person of Prof. Dr. Georgi Todorov for the trust, the moral and financial support they provide for the development of tribology.

I would like to express my special thanks to Prof. Dr. Nyagol Manolov - our teacher and founder of Bulgarian and Balkan tribology, for his creativity, deep motivation and devotion to the ideas and followers of tribology.

I wish you an exciting and fruitful conference!

Prof. Dr. Mara Kandeva,
President of the Society of Bulgarian Tribologists,
Head of the Tribology Laboratory,
at the Faculty of Industrial Technology
Technical University of Sofia

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ДИАГНОСТИКА НА ЛАГЕРИТЕ ЧРЕЗ ГРАПАВОСТТА НА КОНТАКТНИТЕ ЕЛЕМЕНТИ

Вяра ПОЖИДАЕВА, Мара КАНДЕВА, Емилия АСЕНОВА

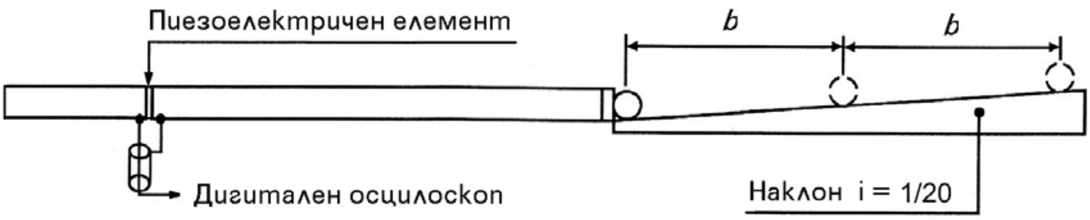
Abstract: *The article proposes an analytical method for fixing the ripple frequency of rolling bearings, resulting of roughness and small defects on working surfaces. The method has been developed for the roller bearings from open-pit mining machines. On the basis of theoretical precondition and test measurements limit values are received for intensity pulses in the vibrosignals as function of bearings wear.*
Keywords: *vibration control, roll bearings, wear, mining, machines*

1. ВЪВЕДЕНИЕ

В реални условия разрушаването на контактните повърхнини се обуславя от комплексни причини предизвикващи едновременното възникване и развитие на редица повреди. В началният стадий на износване обикновено се наблюдава постепенно увеличаване на грапавостта на повърхнините, а след това процесът се задълбочава до възникването на отделни дефекти по тях. Типичен пример в това отношение са търкалящите лагери, които на практика рядко изчерпват ресурса си в следствие на умора на материала. Този факт предопределя потребността от ранна диагностика на процесите на износване в лагерите с оглед на тяхното правилно техническо обслужване и създаване на възможност за тяхната експлоатация до изчерпване на лагерния ресурс.

2. ТЕОРЕТИЧНА ПОСТАНОВКА

В практиката са известни много диагностични подходи, но най-ефективният за диагностика на износването в лагерите се основава на контрола на вибрационния сигнал във високочестотната област (27-35 kHz). В случая се изхожда от обстоятелството, че търкалящият лагер представлява генератор на случайни импулси, които се пораждат при движението на търкалящите тела по лагерните пътечки. Причина за поява на импулсите е грапавостта на контактните повърхности на взаимодействуващите си в маслена среда лагерни елементи. Интензивността на импулсните взаимодействия, както и големината на всеки отделен импулс зависи от дебелината на масленият филм в контактните зони и степента на износване в лагера изразена, чрез грапавостта на повърхнините.
В това отношение публикацията на Sohoel [1] дава възможност да се нормират съответни стойности на интензивността и импулсната последователност предизвикана от неравностите в контакта.



фиг.1. *Теоретичен модел за изследване на физическата същност на еластични ударни вълни*

На базата на модела от фиг.1. се определят следните вибрационни характеристики на единичен ударен импулс, а именно:

$$V = \sqrt{2.g.b.i} \quad (1)$$

където: *V*, [m/s] е скорост на ударен импулс, предизвикан от контакта между две изпъкналости в профила на взаимодействуващите си лагерни елементи;

b, [m] е разстоянието между две последователни изпъкналости в профила;

g = 9,81 m/s^2.

$$T = \frac{R}{(V)^{\frac{1}{5}}}.k_1 \quad (2)$$

където: *T*, [μs] е време на ударното взаимодействие от началото на удара до момента в който вибрационната скорост стане 0;

R, [mm] е радиус на търкалящото тяло;

$к_1$ = 4.5 коефициент установен по емпиричен път.

$$P_{\max} = (V)^{\frac{6}{5}}(m)^{\frac{3}{5}}(R)^{\frac{1}{5}}.k_2 \quad (3)$$

където: P_{max}, [N] е максимална контактна сила (при *V* = 0);

m, [mm^3] е относителна маса на търкалящо тяло, $m = R^3$;

$к_2$ = 1,16 коефициент установен по емпиричен път.

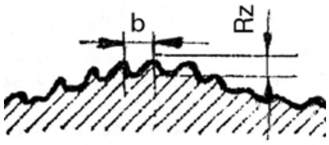
Така определените вибрационни характеристики на единичен ударен импулс позволяват те да бъдат изчислени за различни стойности на износването в границите на нормирани параметри на микропрофила.

За определянето на евентуалният брой на ударните импулси в контактната зона ще се позовем на стандарта за грапавост на повърхнините и по-специално на параметъра “средна стъпка на профила по върховете на грапавините - S”, който окачествява именно разпределението и броя на пиковете спрямо средната линия и се определя като средноаритметична стойност на стъпките b между върховете на профила в границите на базовата дължина ℓ (за лагерни повърхнини ℓ = 0,25 mm.) (фиг. 2)

$$S = \frac{1}{m}\sum_{i=1}^{m} b_i \quad (4)$$

Съгласно определението за грапавост на повърхнини параметъра S се обвързва с параметъра R_Z (височина на грапавините по 10 точки спрямо средна линия) за окачествяване на грапавост, а именно:

$$\frac{S}{R_z} \leq 50 \quad (5)$$



Фиг. 2. *Стъпка на профила по върховете на грапавините*

Съгласно БДС EN ISO 1302 числената стойност на R_Z параметъра за лагерни повърхнини е 1 μm и за да бъде изпълнено условие (5) от същият стандарт избираме числена стойност за b_1 = 0,05 mm. Тогава евентуалният брой на пиковете *q* в базовата дължина може да се пресметне приблизително от:

$$q = \frac{\ell}{b} \tag{6}$$

като за лагер с нормална грапавост на повърхнините броят ще бъде:

$$q_1 = \frac{\ell}{b_1} = \frac{0,25}{0,05} = 5 \text{ бр.,}$$

а за лагер с увеличена грапавост, при максимално лошо качество на повърхността, от стандарта отчитаме b_2 = 0,002 mm и броят на пиковете е:

$$q_2 = \frac{\ell}{b_2} = \frac{0,25}{0,002} = 125 \text{ бр.}$$

Параметърът i – в (1) може да се идентифицира [2] при реален обект с относителното сближение между контактните повърхности x [μm], което за нуждите на нормирането приема две гранични стойности а именно:

$$x_1 \approx 1,54\left(\frac{r}{R_{\max}}\right)^{\frac{1}{5}} .\left(P_c.\theta\right)^{\frac{2}{5}} \text{, μm} \tag{7}$$

сближение при неизносен профил и

$$x_2 \approx 5,4\frac{r}{R_{\max}}\left(c.P_c.\theta\right)^2 \text{, μm} \tag{8}$$

сближение при изчерпан лагерен ресурс определено като критична деформация, съответстваща на прехода на материала към състояние на пластичност.

Означенията във формули 7 и 8 са както следва:

r – среден радиус на закръгление на върховете на грапавините, μm;

R_{max} – най-голямата височина на неравностите на профила в рамките на базовата дължина, μm;

P_c, [N/m^2] – фактическо налягане в лагера определено като отношение между натоварването F и лицето на контактната площадка A_c, определено съгласно теорията на Херц.

$$P_c = \frac{F}{A_c} \tag{9}$$

θ [Ns^2/m^2] - еластична константа на материала на контактните повърхности пресметната чрез коефициента на Поасон μ [Ns/m^2], и модула на еластичност E [N/m^2]

$$\theta = \frac{1-\mu^2}{E} \tag{10}$$

c – коефициент зависещ от формата на върховете на грапавините. За сферична форма, каквато е възприета в случая *c* = 0,55.

В съответствие с класа на точност на търкалящите лагери, опитно установени и изчислени са следните характеристики (Таблица 1)

Таблица 1. *Параметри на грапавостта на повърхнините*

Ra, μm	Rmax, μm	r, μm
0,16–0,08	1,0–0,5	30
0,08–0,04	0,5–0,25	40
0,04–0,02	0,25–0,125	55

Фактът, че вибрационните нива на резонанстните лагерни честоти се обвързват с грапавостта на повърхнините, а също и определението за възприемане на сигнал от точков източник, позволяват да се предположи, че чувствителната част на сферичният накрайник на преобразувателя притежава размери равни на стандартизираната базова дължина ℓ при която се окачествява грапавостта на лагерните повърхнини, а именно ℓ = 0,25 mm. Тогава преобразувателите за контрол на лагери ще регистрират възбудените импулси не от цялата контактна площадка, а само от точковия източник в рамките на базовата дължина ℓ приблизително по линия (с дебелина ~ 1 mm) . При тези предположения размерът на контактната площ за нуждите на настоящото нормиране ще бъде:

$$A_c = n\ell = n(0.25x1) = 0.25n \text{ , mm}^2 \qquad (11)$$

където n е броят на базовите дължини ℓ, които ще преминат през датчика за времето на измерване и събиране на отчети [3]. Същите могат да се определят с помощта на теорията на Херц за всеки отделен лагер, в съответствие с неговата конструкция и работна честота.

ИЗВОДИ

1. Съществува връзка между износването в лагерите и параметрите на високочестотните вибрации.
2. За нуждите на безразрушителния контрол чрез вибрационни измервания е необходимо предварително нормиране на съответни кореспондиращи си стойности на износването и вибрационната характеристика в съответствие с конкретните конструктивни особености на лагерното вграждане.
3. Специално за лагерите от минната механизация, работещи при големи натоварвания и ниски работни честоти, илюстративен параметър за наличния лагерен ресурс е грапавостта на повърхностите на лагерните елементи.
4. Настоящата методика позволява определянето на параметрите на импулсните взаимодействия в лагера по амплитуда и честота, което удовлетворява изискванията за коректен вибрационен контрол.

ЛИТЕРАТУРА

1. SOHOEL E., *A complete set of tools for evaluating the running condition of operating rolling element bearings,* SPM Instrument AB, August, 1994.

2. КРАГЕЛЬСКИЙ И., ДОБЫЧИН М., КОМБАЛОВ В., *Основы расчетов на трение и износ,* Москва, Машиностроение, 1977.

3. КОДНИР Д., *Контактная гидродинамика смазки детайли машин,* Москва, Машиностроение, 1976.

4. MAZIOUD A, IBOS L., KHLAIFI A., DURASTANTI J. F., *Detection of Rolling Bearing Degradation Using Infrared Thermography,* 9th International Conference on Quantitative Infrared Thermography, July 2-5 , 2008, Krakov, Poland

5. BARRET, M., DURASTANTI, J. F., MADANI, K., *Diagnostic vibratoire base sur la transformee en ondelettes,* Congres CNRIUT03, Mai 2003, Tarbes (France).

6. STAIDEL R.F., *An Introduction to Mechanical Vibration,* WILEY, New York, 1989.

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Tribological Journal BULTRIB Vol. 7, 2018
Papers from the 13th International Conference **BULTRIB '18**
25-27 October 2018, Sofia, Bulgaria
Society of Bulgarian Tribologists
FIT – Technical University of Sofia

MECHANOCHEMICAL SYNTHESIS OF ZINC SELENIDE IN INDUSTRIAL MILL FOR PHOTOCATALYTIC DEGRADATION OF AZO DYE

Nina KOSTOVA, Marcela ACHIMOVIČOVÁ, Martin FABIÁN

Abstract: *Nanocrystalline ZnSe was prepared by mechanochemical synthesis in industrial mill from the mixture of Zn and Se powdered precursors. XRD measurements indicate the formation of the cubic modification of ZnSe. An application of the industrial mill verified the possibility of a large-scale mechanochemical production of ZnSe semiconductor at ambient temperature and in a short reaction time. The photocatalytic activity of the mechanosynthesized ZnSe was evaluated by photodegradation of Methyl Orange dye under visible light irradiation.*

Keywords: *ZnSe, industrial vibratory mill, mechanosynthesis, photocatalysis, Methyl Orange*

1. INTRODUCTION

Environmental pollution is one of the greatest problems in the world and consists of three basic types of pollution, namely: air, water, and soil [1]. Wastewater effluents from textile industries are severe threat to environment and human health [2]. The azo-dyes constitute the largest portion present in wastewaters from textile industries. Various technologies have been developed for remediation of dye contaminated colored water such as adsorption, ozonation, photocatalytic processes, biological treatment, etc. Photodegradation is one of the process projected to remove pollutants from the environment [3, 4]. In the past decades semiconductor photocatalysts have attracted considerable attention for a long time in the field of photochemistry because of broad applications in the solving of the environmental problems [5]. Conventional semiconductor photocatalysts are mostly oxides, especially TiO_2 but which can only absorb UV light. Exploration of visible-light photocatalysts with high catalytic activity is currently a hot research topic. Zinc selenide belongs to group of II-IV semiconductors that have been the focus of attention for various applications. The preparation routes of ZnSe have been hydrothermal [6], solvothermal [7], chemical bath deposition [8], combustion synthesis [9], electrosynthesis [10]. De Lima and co-authors were the first to have investigated the ball milling technique for preparation of ZnSe mixture [11, 12].

Mechanochemical synthesis of various chalcogenide semiconductors has been described in the several works [13-17]. This preparation route concerns with the solid state reactions induced by mechanical energy. Gock and co-authors have described the industrial production of nanoscale metal sulfides by means of reactive grinding [18].

The aim of present work was to prepare the nanocrystalline ZnSe by mechanochemical synthesis in an industrial mill in short reaction time. The photocatalytic activity to Methyl Orange azo dye under visible light irradiation was investigated.

2. EXPERIMENTAL PART

The mechanochemical synthesis of ZnSe nanoparticles was performed by milling of the mixture of zinc(97% mean particle size 39 μm, Ites, Slovakia) and selenium powders (99.5%, mean particle size 46 μm, Aldrich, Germany) in the industrial eccentric vibratory mill ESM 656-0.5 ks (Siebtechnik, Germany), according to the following reaction: *Zn + Se = ZnSe.* The reaction is thermodynamically possible because of the negative value of enthalpy change ΔH^0_{298} = - 159 kJ mol^{-1}.

The following conditions were used for mechanochemical synthesis in the industrial eccentric vibratory mill: loading of the mill – material of 5 l milling chamber and balls – tungsten carbide, the balls (30 mm in diameter) with the total mass of 17 000 g, mass of Zn – 45.3 g, mass of Se – 54.7 g, milling atmosphere – Ar, the rotation speed of motor – 960 rpm, the amplitude of the inhomogeneous vibrations – 20 mm and milling time 15 min.

X-ray diffraction measurements were carried out using a X`Pert diffractometer (Philips, Netherlands), working in the geometry with CuKα radiation. The JCPDS PDF database was utilized for phase identification. The crystallite size values of the product was calculated from (111) reflection using Scherrer equation [19].

The specific surface area was determined by the low-temperature nitrogen adsorption method using a Gemini 2360 sorption apparatus (Micromeritics, USA).

The diffuse reflectance UV–vis spectra for evaluation of photophysical properties were recorded in the diffuse reflectance mode and transformed to absorption spectra through the Kubelka-Munk function. A Thermo Evolution 300 UV-vis Spectrophotometer (ThermoScientific, USA), equipped with a Praying Mantis device was used. The reflectance data were obtained relative percentage reflectance to a no absorbing material (spectralon) which can optically diffuse light.

The photocatalytic activity of all samples was determined by photodegradation of organic azo dye Methyl Orange (MO) under visible light illumination. At first, 0.10g of prepared ZnSe was suspended in 100 mL of MO solution (10 mg L^{-1}). The obtained mixture was subjected to stirring in the dark for 30 min to achieve adsorption-desorption equilibrium. Then, the mixed suspension was kept under visible light illumination. At a given time interval, 3 mL of mixed suspension was sampled and centrifuged to eliminate the photocatalyst. The residual concentration of MO was estimated at 463 nm using a SPEKOL 11 (Carl Zeiss Jenna, Germany) spectrophotometer.

3. RESULTS AND DISCUSSION

Fig. 1 shows the X-ray powder diffraction pattern of the mechanosynthesized product formed after 15 min milling in the industrial vibratory mill. The cubic phase was formed.

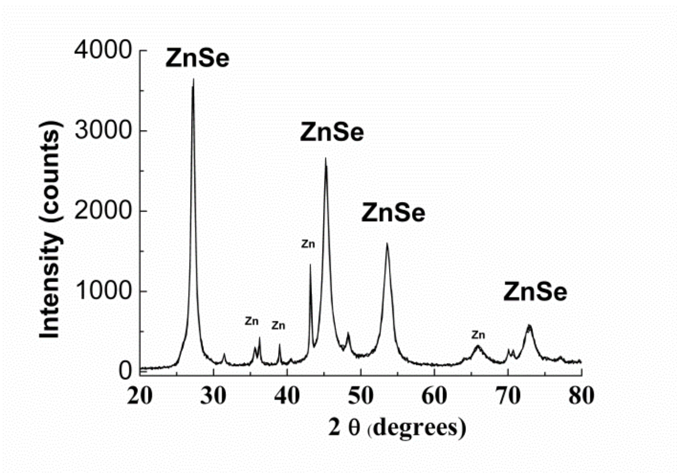

Fig. 1. XRD pattern of mechanochemically synthesized ZnSe in the industrial mill

The XRD analysis of the mechanosynthesized ZnSe product confirmed its nanocrystalline nature. Calculated crystallite size using the reflection of ZnSe (111) plane was 10 nm for prepared nanoparticles and their specific surface area was 2.3 m^2g^{-1}.

The optical properties of semiconductors are related to their band gap energies. Therefore UV-vis diffuse reflectance spectrum of mechanosynthesized ZnSe powder semiconductor was measured and the result is shown in Fig.2. The experimental results indicated that the mechanosynthesized ZnSe powder shows good visible light absorption and remains stable at longer wavelength event up to 1000 nm. This result is in accordance to the color of the sample which was brownish.

The band gap energy was calculated by modified Kubelka-Munk function, F(R) [20]:

$$F(R) = (1-R)^2/2R = K/S, \qquad (1)$$

where K and S are the absorption and scattering coefficients, respectively. The absorption coefficient α is related to the incident photon energy by means of the Tauc's equation [21]

$$\alpha h\nu = C(h\nu - E_g)^{1/2} \qquad (2)$$

where C is proportionality constant and *hv* is the proton energy. The band gap energy was calculated from the slop of graph against photon energy hv by extrapolating the linear fitted region to $(\alpha hv)^2 = 0$ [21] (Fig. 2, inset). The band gap of mechanochemically synthesized ZnSe is 2.3 eV, which is narrower than that of bulk ZnSe (2.7 eV).

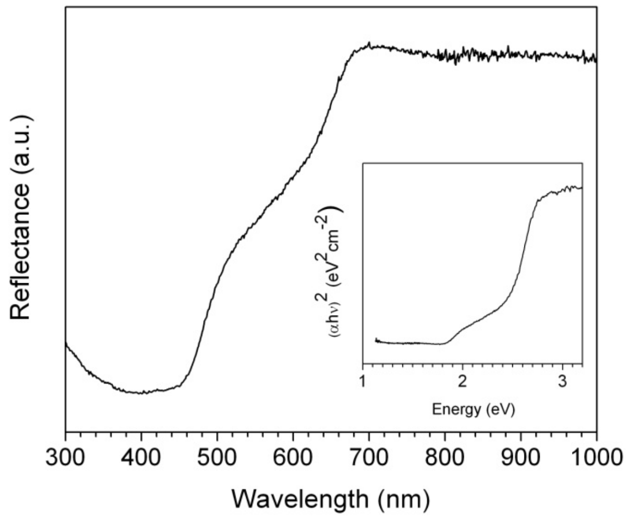

Fig. 2. Diffuse reflectance spectra and plot of $(\alpha hv)^2$ versus photon energy of mechanosynthesized ZnSe.

The photocatalytic activity of mechanosynthesized ZnSe was examined through the degradation of Methyl Orange (MO) azo dye in aqueous solution at various time durations. We decided the MO as a target pollutant because it is good model compound, stable under light irradiation. Dye pollutants are major source of environmental contaminant. Azo dye accounts for over 50 % of total number of dye structures known. These dyes are non-biodegradable and show a relatively high persistence in soils and aquatic systems. The characteristic absorption of the MO dye at λ = 463 nm was selected to monitor the photocatalytic degradation process. The molecule of MO is relatively stable in aqueous solution. The control analyses show that degradation of MO is negligible without visible light irradiation or in the absence of ZnSe photocatalyst.

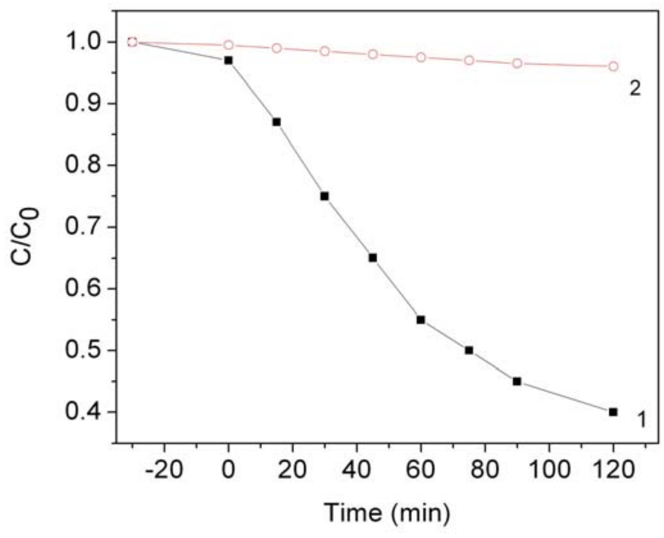

Fig. 3. Photodegradation curves of the MO dye solution under visible light in the presence of mechanosynthesized ZnSe (1) and without photocatalyst (2).

As illustrated in Fig. 3, 60 % of the MO azo dye decomposed after exposure to 120 min under visible light in the presence of the mechanosynthesized ZnSe. The photodegradation of MO under visible light irradiation, catalyzed by the mechanosynthesized ZnSe fits pseudo-first order reaction i.e. ln $C_0/C = kt$, where C_0 and C are the initial and actual concentration of MO, respectively, and k is the apparent rate constant of the degradation. In our experiment k is found to be 3 x 10^{-3} min^{-1}. The linear relationship between lnC_0/C and time τ can be achieved for photodegradation curve of ZnSe (Fig. 4).

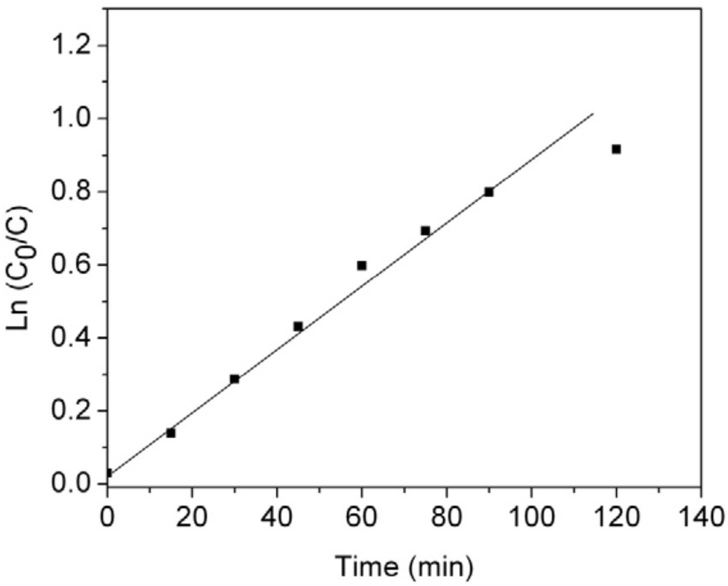

Fig. 4. Degradation kinetic of MO with mechanosynthesized ZnSe under visible light irradiation

The reusability of the ZnSe was also studied. The absorbance spectra of the MO dye solution in the presence of ZnSe with irradiation after 120 min were recorded.

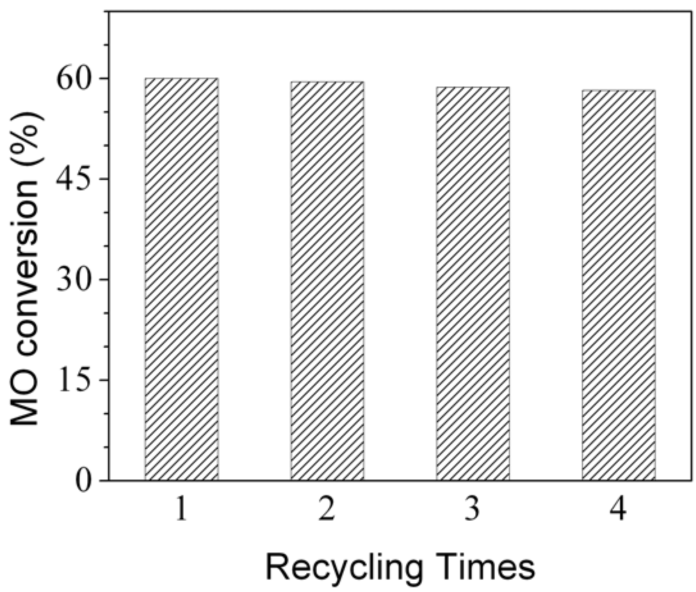

Fig. 5. Recycling activity of ZnSe for MO degradation

After each examination, the ZnSe was immersed into fresh MO azo dye solution of the same concentration for another cycle. This process was repeated 4 times. A slight decrease in the degradation rate was observed and may be attributed to the unavoidable loss of ZnSe into solution during the experiment. The results are given in Fig. 5 and demonstrate that the mechanosynthesized ZnSe can be used as an environmentally safe, effective and recyclable photocatalyst.

The ZnSe absorbs visible light with an energy of $h\nu$ with exceeds the band gap energy of the n-type semiconductor ZnSe to generate electron (e-) and hole (h+) pairs. The energy of the band gap of the mechanosynthesized ZnSe estimated from the DRS is 2.33 eV. It is helpful to generate higher electron and hole pairs. The holes are subsequently trapped by absorbed H_2O on the surface of ZnSe to generate highly reactive hydroxyl radicals (•OH). Correspondingly O_2 acts as an electron acceptor from the conduction band to form a superoxide anion radical (•O_2^-) which combines with protons to generate •OOH. The radical•OH can also be generated from the trapped e- after formation of the radical •OOH. These radicals including •OH and •O^-_2 present extremely strong oxidizing properties and are able to degradation the MO [22]. It is regarded that oxidative degradation of azo dyes such as MO is generally caused by the subsequent attacks of •OH radicals [23]. After addition of •OH radicals to the aromatic group MO the carbon atom bearing the azo bond, followed by the hydroxylated ring is opened to finally yield CO_2 gas, H_2O via oxidation steps, shown as follows *MO + •OH/•O-*$_2$ → *(intermediates)* → CO_2 + H_2O [24]:

4. CONCLUSION

ZnSe nanoparticles have been successfully synthesized by mechanochemically route. The industrial vibratory mill has been proved as the effective reactor for solid state synthesis of ZnSe nanoparticles starting from zinc and selenium as reaction precursors. The final ZnSe material possesses the cubic structure. The mechanosynthesized ZnSe was demonstrated as effective, environmentally safe and recyclable photocatalyst under visible light.

ACKNOWLEDGMENTS

The present work was supported by the Bulgarian Science Fund for financial support by project DNTS/Slovakia 01/2. We would like to thank Dr Y. Karakirova for her help related to MO concentration by SPECOL spectrophotometer.

REFERENCES

1. J. McLaren, I.D. Williams, The impact of communicating information about air pollution events on public health, Sci. Total Environ., **538**, 2015, 478 - 491.
2. L. Pereira, M. Alves: Dyes-Environmental impact and remediation in Environmental Protection Strategies for Sustainable Development, **Vol. 14**, A. Malik, E. Grohmann (Eds). Springer, New York, pp.111-162 (2012).
3. D. Ayodhya, G. Veerabhadram, A review on recent advances in photodegradation of dyes using doped and heterojunction based semiconductor metal sulfide nanostructures for environmental protection, Mater. Today Energy, **9** (1), 2018, 83 - 113.
4. I. Nitoi, P Oancea, L Constantin, M Raileanu, M Crisan, I. Cristea, C. Cosma, Relationship between structure of some nitroaromatic pollutants and their degradation kinetic parameters in UV-vis TiO_2 system, J. Environ. Prot. Ecol., **17** (1) 315-322 (2016).
5. U.I. Gaya, A.H. Abdullah, Heterogeneous photocatalytic degradation of organic contaminants over titanium dioxide: A review of fundamentals, progress and problems. J. Photochem. Photobiol. Chem. C: Photochem. Rev. **9** (1), 2008, 1 - 12.
6. K. Liu, L. Zhang, N. J. Ji, H. Liu, Synthesis and phases of ZnSe prepared by hydrothermal method. Optoelectronics and Advanced Materials, Rapid Communications, **8** (9-10), 2014, 873 - 875.
7. Y. Zhang, C. Hu, B. Feng, X. Wang, B. Wan, Synthesis and photocatalytic property of ZnSe flowerlike hierarchical structure. Appl. Surface Sci., **257**, 2011, 10679 - 10685.
8. S. Thirumavalavan, K. Mani, S. Sagadevan, A study of structural, morphological, optical and electrical properties of zinc selenide thin film, Mater. Today: Proceed, **3**, 2016, 2305 - 2314.
9. G. Liu, X. Yuan, J. Li, K. Chen, Y. Li, L. Li, Combustion synthesis of ZnSe with strong red emission, Mater. Design, **97** (1), 2016, 33-44.
10. Y.G. Gudage, N.G. Deshpande, A.A. Sagade, R. Sharma, Room temperature electrosynthesis of ZnSe thin films, J. Alloys Comp., **488**, 2009, 157 - 162.
11. J.C. De Lima, V.H.F. dos Santos, T.A. Grand,: Structural study of the ZnSe system by ball milling technique. Nanostruct. Mater., **11** (1), 1999, 51 - 57.
12. J. Baltazar-Rodriges, J.C. de Lima, C.E.M. Campos, T.A. Grandi, Temperature effects on mechanically alloyed nanometric ZnSe powder, Powder Technol., **189** (1), 2009, 70 - 73.

13. P. BALAZ, M. BALAZ, M. ACHIMOVICOVA, Z. BUJNAKOVA, E. DUTKOVA, Chalconide mechanochemistry in materials science: insight into synthesis and applications (a review), J. Mater. Sci., **52** (20), 2017, 11851 - 11890.
14. M. ACHIMOVICOVA, N. DANEU, E. DUTKOVA, A. ZORKOVSKA, Mechanochemically synthesized cobalt monoselenide: structural characterization and optical properties. Appl. Phys. A-Materials Science & Processing, **123** (3), 2017, Article Number 154.
15. M. BALAZ, E. DUTKOVA, Z. BUJNAKOVA, E. TOTHOVA, N.G. KOSTOVA, Y. KARAKIROVA, J. BRIANCIN, M. KANUCHOVA, Mechanochemistry of copper sulfides: Characterization, surface oxidation and photocatalytic activity, J. Alloys Comp., **746**, 2018, 576-582.
16. E. DUTKOVA, M. CAPLOVICOVA, I. SKORVANEK, M. BALAZ, A. ZORKOVSKA, P. BALAZ, L. CAPLOVIC, Structural, surface and magnetic properties of chalcogenides Co_9S_8 nanoparticles prepared by mechanochemical synthesis, J. Alloys Comp., **745** , 2018, 863-867.
17. M. ACHIMOVICOVA, P. BALAZ, Nanocrystalline metal selenides: Mechanochemical synthesis and utilizable properties pp. 71-122 (Book Chapter) *in* Milling: Fundamentals, Processes and Technologies (M. Ramirez Ed.) ISBN-13: 978-1634830225, Nova Science Publishers, Inc. New York (2015).
18. M. ACHIMOVICOVA, P. BALAZ, J. DURISIN, N. DANEU, J. KOVAC, A. SATKA, A. FELDHOFF, E. GOCK, Mechanochemical synthesis of nanocrystalline lead selenide: industrial approach, Intern. J. Mater. Res., **102** (4), 2011, 441-445.
19. H.P. KLIGG, L.E. ALEXANDER: X-Ray Diffraction Procedures, Wiley, New York, 1954
20. S. VALENCIA, J.M. MARIN, G. RESREPO, Study of the ban gap of synthesized titanium dioxide nanoparticles using the sol-gel method and hydrothermal treatment, Open Mater. Sci. J., **4** (1) 9-14 (2010).
21. J. TAUC, R. GRIGIROVIC, A. VANCU, Optical properties and electronic structure of amorphous germanium, Phys. Status Solidi, **15**, 1966, 627 - 637.
22. N.G. KOSTOVA, M. FABIAN, E. DUTKOVA, M. BALAZ, M. SHIPOCHKA, Characterization of mechanochemically synthesized N-doped TiO_2, Bulg. Chem. Commun., **50**, Special issue H, 2018, 122 - 129.
23. A.N. OKTE, O. YIMAZ, Characteristics of lanthanum loaded TiO_2-ZSM-5 photocatalysts: Decolorization and degradation processes of methyl orange, Appl. Catal. A: General, **354,** 2009, 132 - 142.
24. W. ZHANG, Z. YANG, X. WANG, Y. ZHANG, X. WEN, Large-scale synthesis of β-MnO_2 nanorods and their rapid and efficient catalytic oxidation of methylene blue dye, Catal. Commun., **7** (6), 2006, 408 – 412.

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Tribological Journal BULTRIB Vol. 7, 2018
Papers from the 13th International Conference **BULTRIB '18**
25-27 October 2018, Sofia, Bulgaria
Society of Bulgarian Tribologists
FIT – Technical University of Sofia

FRICTION AND WAVE EFFECTS IN GEOLOGICAL PROCESSES IN THE EARTH`S CRUST

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Abstract: *Seismic-tectonic shear zones of the Earth`s crust produce an enormous amount of kinetic energy as a result of inter-block friction and seismic waves. The kinetic energy causes destructive deformations and activation of the rock system and its shear zones, which transform later into constructive creative processes, e.g. crystallization in new rocks of the damaged broken mass.*
Keywords: *friction process evolution, friction and waves, geotribology, seismic waves, energy*

Резюме: *Сеизмотектонските зони на срязване в Земната кора произвеждат огромно количество кинетична енергия вследствие на междублоковото триене и сеизмичните вълни. Кинетичната енергия причинява деструктивна деформация и активизиране на скалната система, по-късно трансформирана в констуктивни съзидателни процеси като кристализация на повредената разбита маса в нови скали.*
Ключови думи: *еволюция на процеса на триене, триене и вълни, геотрибология, сеизмични вълни, енергия*

1. INTRODUCTION

The Earth`s crust is a living organism in a state of eternal movements. Tectonic processes like earthquakes, collision, folding, faulting, thrusting, subduction and obduction provide formation of a great number of shear zones of friction, which appear on various scale level: mega - transcontinental zones, mesozones observed on outcrops, microzones, and submicro- or nanozones in the crystal lattice. Various triboprocesses develop in these zones during tectonic movement.

A wave effect - a specific derivative form of friction outside the shear zones manifested as eclogitization on the serpentinites, was noted [1,2] in the Eastern Rhodope Mountain. The shear zones of friction and wave action, as well as the changes induced by them on the rocks are object of research and study of the interdisciplinary science geotribology [3-6].

Geotribology has been developing for more than ten years in the Society of Bulgarian Tribologists as a branch of the Overall Tribology and a particular trend in the group of Earth's sciences studying the transformation of rocks in seismic-tectonic zones under the influence of kinetic energy [5-7]. Geotribology traces the energy link between destructive and constructive processes in the Earth's crust.

The aim of the paper is to present a brief review on friction and wave effects on the geological processes in the Earth's crust based on the energy balance of the interaction of bodies during friction.

2. TRANSFORMATION OF ENERGY DURING FRICTION

Friction - the resistance to movement – is a global natural phenomenon of energy transformation and dissipation during the joint work of surfaces in contact. Numerous experimental and theoretical studies explore the effect of friction on the physical-chemical properties of matter and formulate the thermodynamic principles of tribology. According to the energy model, friction is considered as process of transformation and dissipation of energy and process of elasto-plastic deformation localized in the surface layers of the interacting bodies [8-10].

Friction results of two opposite simultaneous trends: Accumulation of potential energy by the deformable contact and release (dissipation) of that energy. The first one defines the effect of deformation and damage; the second one - the heat effect of friction. Based on the energy balance equations of friction and the structural-energy relationships in the contacting surfaces evolution, the adaptive-dissipative character of the evolution of tribosystems can be tracked [9,10] (see Fig. 1). It reflects the competitive (dialectical) nature of friction, the variable friction surfaces compatibility and the nonlinear dynamics of friction evolution. Friction evolution goes through stages.

According to the thermodynamic balance principles of friction, the evolution curve has a number of principal points (1 to 5) of the transient stages of the tribosystem. Between these points are located the most characteristic areas of tribosystem's nonlinear behavior, as follows:

0-1- section of static friction and deformation strengthening; 1 – limit deformation strengthening point; 1-2 – stage of pumping of excessive energy; 2 – point of seizure and transition from external to internal friction (critical non-stability); 2-3 – stage of dissipative structures formation (heat fluctuation in the friction volume); 3 – minimum compatibility point; 1-2-3 – self-organization area; $3-4^1$ - stage of compatibility; 4 - point of abnormal low friction; 5 – point of heat seizure. The points of synergy are the points of specific equilibrium states of the contact. Between them are the sections of structural-energy transformation. Three main sections – a triadic friction process evolution, are observed: Deformation/destruction (under external energy impact); Culmination – transition from external to internal friction; and Regeneration of the system at a new level and with new structures (formation of dissipative protective structures).

Self-organization emerges with the fulfillment of a synergy principle: availability of the combined (joint) effect and balance between the two opposite trends: accumulation of internal energy by the deformable contact body and release/dissipation of energy with forming of dissipative structures.

The evolution of the contact follows the development of opposite trends immanent in the friction process, i.e. the transformation of energy (degenerative /negative processes and constructive /regeneration processes), aiming an optimistic end – preservation of the system on a new level with new structures.

Analogy with above model and general diagram of the structure-energy evolution of frictional contact and to the considered energy approach is developed below concerning friction processes in the frictional zones, i.e. the geotribozones between blocks of rock in the Earth's crust (see Fig. 2) [6].

3. GEOTRIBOLOGICAL PROCESSES IN THE SHEAR ZONES OF FRICTION

3.1. Evolution of the frictional contact between rocks. Energy influence inside the tribozones.

Being a branch of tribology and an interdisciplinary science of the group of geosciences, geotribology considers the contact interaction during friction between blocks or layers in the seismic-tectonic zones within the Earth's crust and the transformation of rocks and minerals there under the influence of tectonic energy. Tectonic zones in the Earth's crust emerge always with fracture between blocks. When the tectonic stresses in a given section reach critical values, the rock blocks that have been in a state of rest or preliminary displacement are brought to a relative motion. The initial moment of relative motion associates with a sudden and abrupt change of the state of rest to state of movement and is manifested as a shock of destructive effect, transforming the tectonic zones into seismic tribological zones. An immense amount of energy is produced in the friction zones, which is completely sufficient to ensure the high temperature and pressure required for crystallization of new mineral associations, e.g. for the HP/UHP eclogite crystallization [5].

Similarly to the general structure-energy evolution of friction (see Fig. 1), three main branches of friction process evolution are observed in the geotribozones (see Fig. 2): 1. Deformation/destruction and melting of rock in the interface of the contacting blocks (under tectonic energy impact); 2. Culmination – maximal activity of triboprocesses and transition from external to internal friction; 3. Regeneration/crystallization of the system at a new level and with new structures [6].

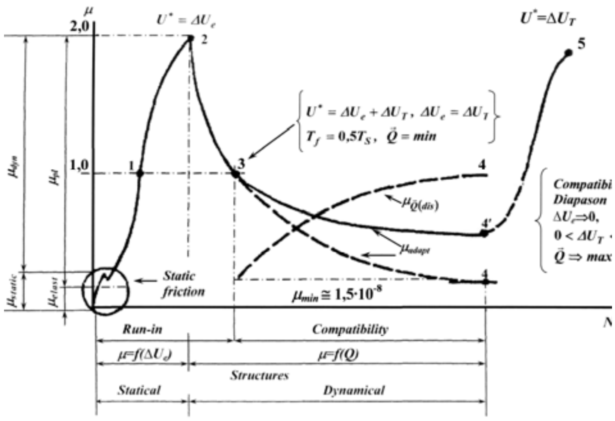


Fig.1. Evolution curve: General diagram of the structure-energy evolution of a tribosystem (a deformable frictional contact volume) [9]

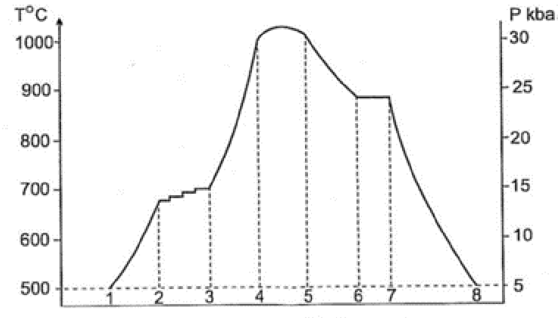


Fig. 2. Termobaric scheme of development of tribological process

1 – 4 destructive stage with phases:
1-2 deformation, 2-3 disintegration, 3-4 activation;
4 – 5 culmination stage; 5 – 8 constructive stage with phases: 5-6 cooling,crystallization, 7-8 diaphthoresis

Evolution of the contact begins with the **first, destructive stage;** it is progressive stage as sequence of development. Destruction starts with elastic and plastic deformation, followed by brecciation, cataclasis and mylonitization of the rocks. Point, line and planar defects emerge even in the mineral lattice. The inner dislocations and shift of the crystal structure lead to fracture and fragmentation of the minerals. In an advance stage of deformation, the crystal chemical bonds tear to complete decomposition of the minerals, reaching molecular and atomic level till to exoemission of ions and electrons and to formation of melts.

At the **second stage** of maximal activity of triboprocesses, specific thermodynamic circumstances in the tribozone are established. The kinetic energy, supplied by tectonic movements, transforms to thermal one. The internal energy increases, the free energy decreases, the entropy and enthalpy also change. Due to all mechano-chemical and tribochemical processes, the temperature, pressure and chemical activity increase considerably. The cumulated effect of tribo-processes can provoke extremely high temperature and pressure in the narrow closed space of the tribozone. The high concentration of energy into confined space accompanied by a high velocity of friction can for a moment bring a temperature "explosion", so in an instant the temperature increases to more than 1000°C [5].

A specific feature of the triboprocesses is the preservation of higher temperature and pressure only in the narrow space of a tribozone while beyond its boundaries temperature and pressure decrease rapidly. The tribozone may be considered as a closed or semiclosed thermodynamic system comparable to an autoclave in which chemical reactions reach local equilibrium.

The **third stage** is regressive regarded as sequence of evolution and constructive from the point of view of creation of new mineral assemblages. The supply of tectonic energy has stopped, however the system is still charged with a high amount of stored energy. The tribozone still does not exchange mass but it is no more closed and exchanges energy with the environment. Temperature and pressure begin to decrease with a speed depending on the depth level of the tribozone, although in any case much slower than the rapid, even in some cases, flash increase during the progressive stage of the tribological process. This is a stage of new crystallization and consolidation of the tectonic zone. Upon reaching the crystallization point, the activated mass is structured at the appropriate temperature and pressure, which are still much higher than those in the environment. The newly crystallized minerals are normally high-thermobaric anhydrous silicates and oxides, with a dense crystal lattice. The melts crystallize in new high-thermobaric mineral assemblages containing sometimes micro-diamonds and coesite. In the shallow levels of the Earth's crust, glassy pseudotachylites may occur due to a rapid cooling of the melts, however, going deeper, the new rocks show a granoblastic structure. The velocity of structure growth is much lower than that of the rate of melting. Temperature T and pressure P begin to decrease with a speed depending on the depth level of the tribozone, and yet anyways much slower than the rapid, even flash increase during the progressive stage of the tribological process.

At the same time, out of the tribozone the country rocks are composed of lower thermobaric minerals. The newly crystallized high thermobaric mineral associations are synchronous but heterofacial to the mineral assemblages of the host rocks.

The entire thermodynamic situation in the Earth's crust is changed by the evolution of geotribological friction processes. Illustration is given further with the example of fault/leap shear zone formation and the change of the thermodynamic situation under the influence of tectonic energy (see Fig. 3).

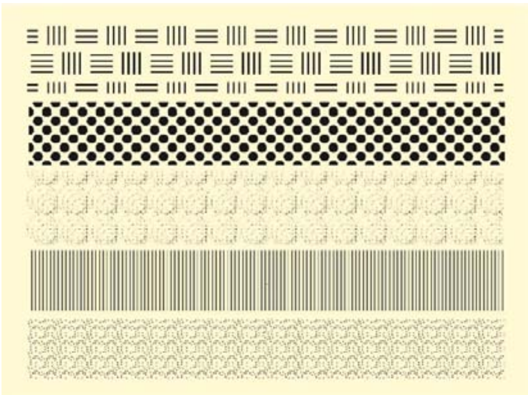


Fig. 3a - the rock system before tectonic movement zone; terrestrial layers of different composition, isotropic T and P distribution

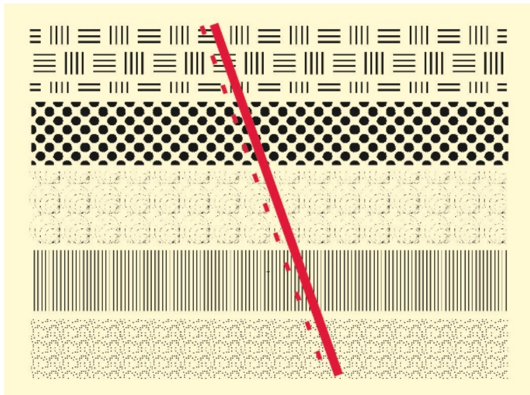


Fig. 3b, c - tectonic situation; tectonic zone with energy gathering

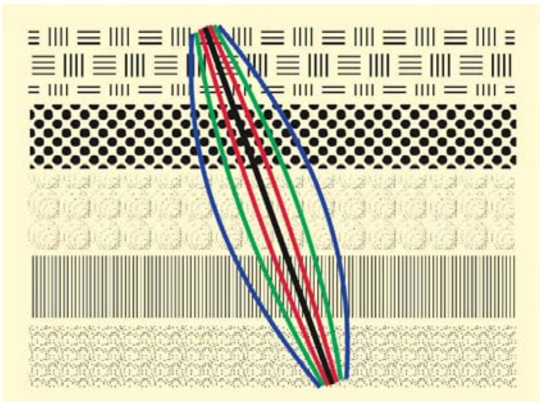


Fig. 3c– additional latent energy in the zone

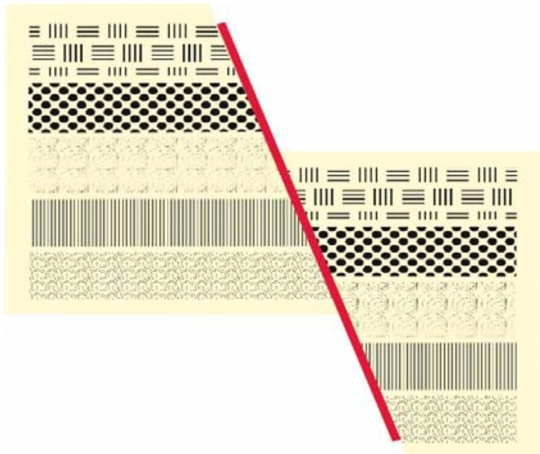


Fig. 3d – result: tectonic movement: a faulting, movement down, the layers are dislocated, new thermodynamic situation, anisotropic distribution of T and P

It follows from the foregoing considerations that a solid mass forms out of melt during the process of crystallization during the constructive stage. It is significant to note that crystallization may also take place as rapid restructuring under the tectonic energy impact, with fast passage through the individual stages and practically without forming a melt. Both cases prove that the friction process evolution regarded through the model of synergy and energy transformation has led to an optimistic trend - preserving and extending the life of the system with its components of new mineral structures.

3.2. Energy influence outside the tribozones. Wave impact.

Friction–vibration interactions refer to a wide variety of dynamic phenomena in mechanical systems consisting of a sliding interface. The interactions between friction and vibrations could substantially influence either the vibrations of mechanical systems, or the friction, or both. On one hand, friction in a dynamic system with a sliding interface has the role of exciting vibrations; on the other hand, the vibrations of the system and the variation of normal forces affect the real contact area and interface properties, and thus the friction itself. A related area is also the friction-induced vibration [11-13]. In a broad sense, friction and vibration are interactive and coupled. Friction influences vibration and friction is also influenced by the vibrations of the dynamic systems within which they are generated.

The action of one body sliding on the surface of another can cause the propagation of elastic waves. These waves can, in turn, affect the observed friction behavior. Such waves can be in different forms (see Fig. 4). An example is the elastic interface wave, which is qualitatively similar to a surface wave that can exist on the free surface of an elastic body, e.g. a water surface. The existence of such waves is believed to have also an effect in geotribology.

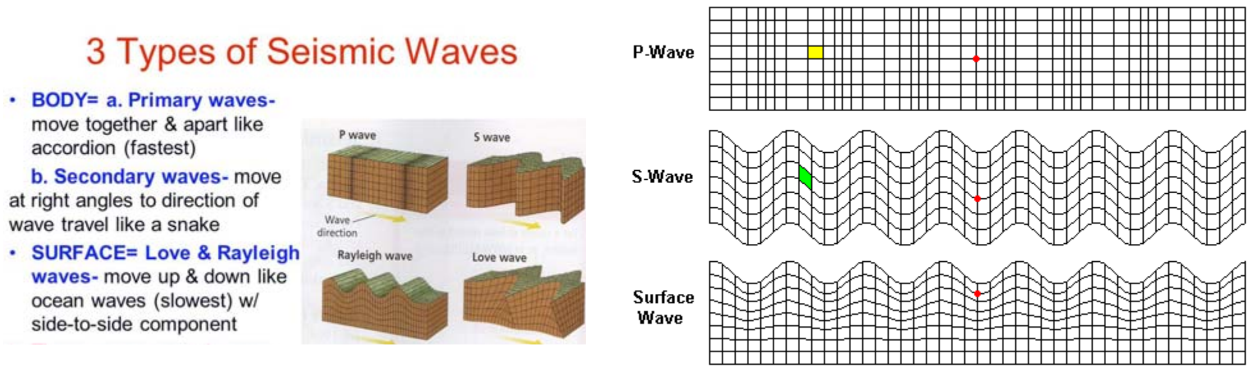


Fig. 4. Types of seismic waves [15]

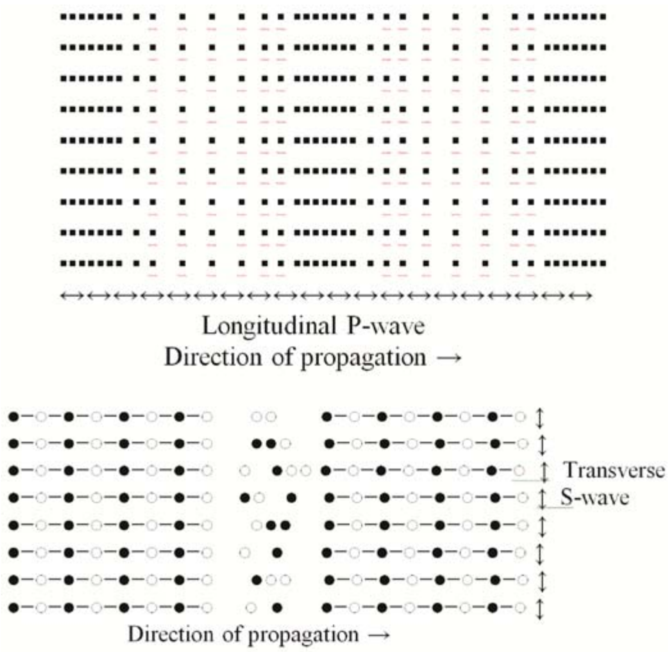


Fig. 5. Scheme of a longitudinal P-wave with zones of dilatation and compression, and of a transverse S-wave

An important fact is that the tectonic energy influences not only directly the friction between rock blocs in the tribological zones but also outside them. It is known from the geophysics that the friction in its three modifications: sliding, rolling and striking/impact, produces mechanical waves, e.g. seismic waves. Propagating **outside** the contact zone, they cause mobilization and vibration of the particles **in** the contact zone. The component particles start to fluctuate around their equilibrium positions.

The seismic-tectonic event provides shock body waves, which propagate as a longitudinal P-wave (primary compression wave) and a transversal shear S-wave (see Figs. 4 & 5). Longitudinal P-waves form rhythmic zones of dilatation and compression, which result in rarefaction and condensation of particles. The second type – S wave or secondary transverse shear wave is slower than the P-wave. The particles fluctuate in two directions: one perpendicular to the first ones and the other to the direction of propagation (see Fig. 5) [1,14].

The mechanical vibrations and waves caused by friction, lead to deformation and instabilities in the components of a tribosystem. Thanks to the energy of tectonic process in geological systems, vibrations and seismic waves from outside the contact zone affect friction in the contact between geological plates and result in further instabilities and dynamic behavior in bulk and contact zones. On the other hand, waves caused by friction have also reverse influence upon the contact intensifying the instabilities in the contact system.

The evolution of friction influences mechanics and thermodynamics, as well as the whole energy conditions of the Earth's crust.

4. CONCLUSION

1. Friction is a global process of joint action of two surfaces in contact. Issues of the energy approach to friction point out that synergy (joint action) of the two frictional surfaces activates the mechanisms of transformation and dissipation of their external motion energy with balance of the joint action of two interrelated and opposite tendencies: accumulation of internal energy and its release/dissipation with forming of dissipative structures.

2. Geotribology is extremely favorable for exploring friction on mega, meso, and micro level scales. The paper highlights the energy relation of the destructive and constructive/regeneration processes during friction in the shear zones/the geotribozones between blocks of rock in the Earth's crust, and the formation of new mineral assemblies. The thermodynamic anisotropy in the Earth's crust is emphasized. The evolution of friction influences mechanics and thermodynamics situation of the Earth's crust.

3. The paper pays special attention to the effect of waves and seismic waves inside and outside the geotribozones on the processes in the Earth's crust.

4. Above analyses lead to new hypothesis about the genesis of some rear rock species.

REFERENCES

1. KOZHOUKHAROVA, E. Eclogitized layered serpentinites in the East Rhodope block. – *C. R. Acad. Bulg. Sci., 49*, 6, 69–71, 1996
2. КОЖУХАРОВА Е. Ритмична приконтактна кристализация. - Сп. Контакти, том 17, 02, (106), изд. ТЕМТО, София, 2017, pp 9-13 (in Bulgarian with an English abstract)
3. ZHANG SIWEI, WANG HONGBO, Geotribology – The Application and Progress of Tribology in Geoscience, Earth Science Frontiers, 2002
4. STACHOWIAK GWIDON, BATCHELOR ANDREW, Engineering Tribology, 4th edition, Butterworth-Heinemann, September 2013
5. KOZHOUKHAROVA E., *Application of Tribo-principles in Geology. An example for Tribochemical Genesis of Eclogites*, 6th Intern. Conference on Tribology BALKANTRIB, Sozopol, Bulgaria, 2008

6. KOZHOUKHAROVA, E. Geotribology – a new view on the tectonometamotphism. – *R.Bul. Geol. Soc., 77*, 2-3; 51-60, 2016
7. КОЖУХАРОВА Е., АСЕНОВА Е., Геотрибология: интердисциплинарност, енергийни и синергийни ефекти в трибозоните на земната кора. **-** Сп. Контакти, том 17, 04, (108), изд. ТЕМТО, София, 2017, pp 3-15 (in Bulgarian with an English abstract)
8. ФЁДОРОВ С.В. Основы трибоэргодинамики и физико-химические предпосылки теории совместимости. – Калининград.: КГТУ, 2003 (in Russian)
9. FEDOROV S.V. Energy balance of friction and friction coefficient in energetic interpretation, 14th Int. Conf. SERBIATRIB'15, Belgrade, 2015, pp. 563-571
10. FEDOROV S.V., ASSENOVA E. Synergy and Self-organization in Tribosystem's evolution. Energy Model of Friction. 2018 *IOP Conf. Ser.: Mater. Sci. Eng.* **295** 012028
11. ADAMS G.G. Contacts Involving Wave Propagation. In: WANG Q.J., CHUNG Y.W. (eds) Encyclopedia of Tribology, Springer, Boston, MA, 2013
12. Friction-Induced Waves. In: WANG Q.J., CHUNG Y.W. (eds) Encyclopedia of Tribology, Springer, Boston, MA, 2013
13. NOSONOVSKY M., ADAMS G.G., Dilatational and shear waves induced by the frictional sliding of two elastic half-spaces. Int. J. Eng. Sci. **39**, 1257–1269, 2001
14. KOZHOUKHAROVA, E. Eclogitization of serpentinites into narrow shear zones from the Avren syncline, Eastern Rhodopes. – *Geochem., Miner. and Petrol*., 35, 29–46, 1998 (in Bulgarian with an English abstract)
15. UDIAS A., BUFORN E., Principles of seismology, Cambridge University Press, 2017

Tribological Journal BULTRIB Vol. 7, 2018
Papers from the 13th International Conference **BULTRIB '18**
25-27 October 2018, Sofia, Bulgaria
Society of Bulgarian Tribologists
FIT – Technical University of Sofia

ИЗСЛЕДВАНЕ НА ИЗНОСОУСТОЙЧИВОСТТА НА ВИСОКОАЗОТНИ ХРОММАНГАНОВИ СТОМАНИ

INVESTIGATION OF THE WEAR-RESISTANCE OF HIGH NITROGEN CHROME-MANGANESE STEELS

Христо АРГИРОВ, Явор ЛУКАРСКИ, Сашо ПОПОВ

Abstract: *The wear-resistant of high nitrogen (till 1% N) chrome-manganese austenitique steels contain 10% Mn, 25% Cr and silicon and vanadium as perspective wear-resistant material is investigated. Increasing of the wear-resistant of the investigated high nitrogen austenitique steels is established thanks to considerable strengthening to the solid solutions and to the deformational strengthening. By the values of the wear-resistant in the conditions of abrasive wear the high nitrogen chrome-manganese steels with Si are of the level of the conventional steels. In the conditions of rolling friction the high nitrogen chrome-manganese steels essentially exceed the nitride ferromagnetique 38CrMoAl steel and the nonmagnetique aged 40Mn14Ni9Cr3AlV steel.*
Keywords: *wear-resistant, high nitrogen steels, abrasive wear, rolling friction*

5. ВЪВЕДЕНИЕ

Едно от направленията за решаване на стратегическия проблем с удължаването на работния цикъл на индустриални машини и инструменти е замяната им с такива, произведени от нови или подобрени материали с повишени експлоатационни свойства [1]. Както е известно, качествената металургия е металургия на стомани и сплави с повишени експлоатационни свойства. Тя позволява създаването на нови или подобряване на използвани до момента стомани и сплави със специални свойства. Новите стомани и сплави притежават необходимия комплекс от механични и физични свойства, като превъзхождат свойствата на конвенционалните марки стомани. Благодарение на повишения комплекс от свойства, от една страна, и от друга-благодарение на понижаването на енергийните, на материалните и на другите разходи за производство, стоманите имат ресурс за дългосрочна работа. Едно от направленията в развитието на качествената металургия е металургията под налягане. Това е метод за получаване на нови стомани и сплави под налягане по-високо от атмосферното. В Института по металознание, съоръжения и технологии с център по хидро и аеродинамика „Акад. А. Балевски“ към Българска академия на науките (ИМСТЦХА-БАН) са създадени теоретични основи в областта на легирането със свръхравновесни концентрации азот и създаването на нов клас стомани-високоазотни стомани и технологии за тяхното производство по методите на металургията под налягане [2]. В основата на технологичните концепции са заложени оригиналните български методи за леене с противоналягане (МЛП) и електрошлаково претопяване под налягане (ЕШПН). Методите МЛП и ЕШПН имат основни предимства при производството на стомани и легирането им с азот: азотът се разпределя равномерно в обема на блока, тъй като се въвежда в течната вана, която интензивно се разбърква и се хомогенизира; възможност за точно регулиране на концентрацията на азота; замяна на скъпи легиращи елементи (никел); плавно и равномерно запълване на кокилата с метал. В следствие на технологичното налягане се произвеждат качествено нови в сравнение с класическото разливане блокове: с подобрена структура, висока плътност и по-малка мъртва глава; универсалност при получаване на различни марки легирани стомани, особено в съчетание с ЕШПН [3].

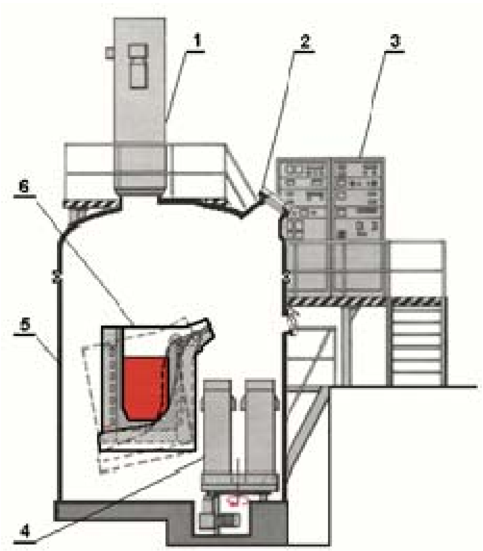
С наличната лабораторна база в съчетание с научния и технологичния потенциал в ИМСТЦХА-БАН са създадени различни нови марки стомани с повишено съдържание на азот и технологии за тяхното производство: бързорежещи, горещощампови, студенощампови, конструкционни и други. Доказано е, че високоазотните стомани притежават между 30 и 150% по-високи механични показатели в сравнение с безазотните аналози. Така например, за режещи инструменти, изработени от високоазотната стомана Р6А2М5 (аналог на Р6М5, DIN S 6-5-2) е установено повишение на експлоатационните показатели от 38 до 100%. Чрез леене под налагане (или с противоналягане) могат да се произвеждат немагнитни хромманганови стомани (включително дисперсионно-твърдеещи), съдържащи до 35% Cr, 20% Mn, 4% V, 3% Si и 1% N [2, 4].

Увеличеният експлоатационен ресурс на подложените на триене елементи на машини и инструменти е свързан с проблема за повишаване на износоустойчивостта на използваните аустенитни стомани. Един от ефективните методи за повишаване на износоустойчивостта на стоманите е азотирането. Използваните в промишлеността високотемпературни режими на азотиране ($t_{азот}$>650°C) осигуряват получаване на достатъчна дълбочина на твърдостта на повърхностния слой, но довеждат до понижаване на якостта или окрехкостяване на сърцевината на детайла и, като следствие, до понижаване на техния експлоатационен ресурс. Износоустойчивостта на много конструкционни стомани е пряко свързана с тяхната якост (твърдост), която съществено зависи от химическия състав на стоманите. Благодарение на значителното уякчаване на твърдите разтвори и на деформационното уякчаване, високоазотните аустенитни стомани са перспективни като износоустойчив немагнитен материал. Уякчаващото действие на азота превишава това на хрома или мангана. Зависимостта на якостта на високоазотните аустенитни стомани от концентрацията на азота има линеен характер.

Цел на настоящата разработка е изследване на износоустойчивостта на високоазотни хромманганови стомани като перспективен износоустойчив материал.

6. ЕКСПЕРИМЕНТАЛНА ЧАСТ

Експерименталните състави са получени в ИМСТЦХА-БАН на инсталация за производство на азотни и високоазотни стомани от най-различни класове на фирмата Leybold Heraeus-Германия [2]. Производственият агрегат представлява индукционна пещ с тигел за стопяване на стомана в количество до 10 kg с възможност за работа под вакуум, при атмосферни условия и под налягане до 3 MPa. Схема на пещта е показана на Фиг. 1, а общ вид на инсталацията на Фиг. 2. Инсталацията позволява обемно насищане на стоманите с азот, като легирането с азот се осъществява чрез твърди азотирани феросплави (азотоносители). В зависимост от марката стомана се достигат всички желани за стоманодобиването концентрации на азота. По този начин се заменят скъпи легиращи елементи и се получават стомани с подобрени или нови служебни свойства.



Фиг. 1. Схема на инсталация за леене под азотно налягане: 1 - шлюзова камера; 2 - отвор за наблюдение; 3 - пулт за управление; 4 - форма за леене; 5 - автоклав; 6 - индукционна пещ

Фиг. 2. Общ вид на инсталация за получаване на стомани с блок за управление

Изследвана е износоустойчивостта на високоазотни (до 1% N) аустенитни стомани, съдържащи 10% Mn, 25% Cr и различно количество силиций и ванадий: 3%Si, 1%V (състав 1); 3% Si (състав 3); 2% Si (състав 4). Стоманите са произведени в ИМСТЦХА-БАН в съществуващата инсталация за индукционно топене при свръхравновесно налягане на азота. Слитъците са пресовани при 1180°C на заготовки, които са закалявани от 1150°C. Стоманата, съдържаща ванадий, след закаляване е подложена на стареене при 650°C в продължение на 10 h.

Изпитванията на абразивно износване са проведени в Института по металургия и материалознание „А. Байков“ (ИМЕТ-РАН) на машина за триене за високи контактни налягания по схемата „въртяща се ролка-плъзгач” със смазка вретенно масло. Като контратяло е използвана ролка от стомана 100Cr6, термообработвана до твърдост HRC-63. Скоростта на въртене на ролката е постоянна величина и равна на 0,5 m/s. Общото времетраене на изпитването е 20 min. Натоварването постепенно е доведено до 1 kg, сработването на контактните повърхности продължава 5 min, след което натоварването е увеличено до 2 kg. Контактното налягане при това е 62 kg/mm^2. Износването на образеца е определяно по стойностите на деформируемото петно (или петното на съприкосновението). Коефициентът на триене е определян по формулата $f_{тр}$=F/P, където F-сила на триенето; P-сила на нормалното налягане.

Стендовите изпитвания в условията на триене при търкаляне са проведени при въртене в противоположна посока на двойка ролки (диаметър 28,7 mm) със скорост 360 и 425 об/min и специфично приплъзване 15% със смазка МС-20. При всяко натоварване образците са изпитвани в продължение на 40 h. Износването е определяно по загубата на теглото [5]. Едновременно с изследваните стомани са изпитвани контролни образци от феромагнитната износоустойчива стомана 38CrMoAl, от стареещата аустенитна стомана 40Mn14Ni9Cr3AlV и нестареещата аустенитна стомана X10CrNiTi 18 9, DIN 1.4541.

3.ПОЛУЧЕНИ РЕЗУЛТАТИ И АНАЛИЗ

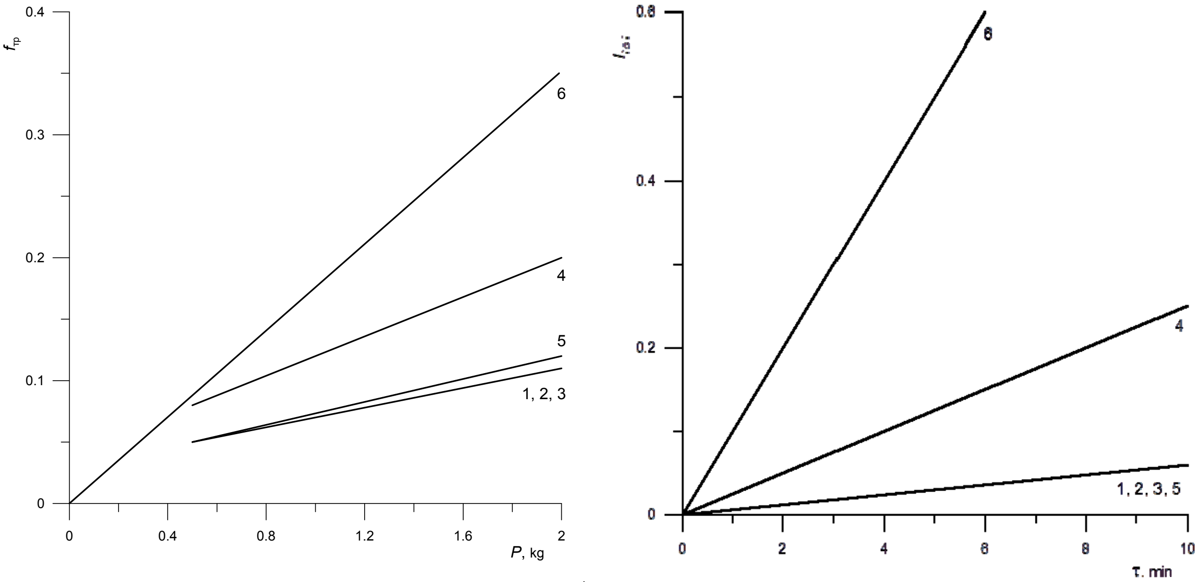
Получените експериментални резултати за стойностите на износването и на коефициента на триене в условията на абразивно износване са представени в Таблица 1.

Таблица 1. Износоустойчивост и микротвърдост на аустенитни стомани след изпитване на абразивно износване

Състав №	Стомана	Обработка	f_{mp}	Площ на износване, mm	Микротвър-дост
1	CrMnN, 3% Si 1% V	закаляване	0,130	2,48	435
2	CrMnN, 3% Si,1% V	закаляване +стареене	0,124	0,69	460
3	CrMnN, 3% Si	закаляване	0,125	3,02	458
4	CrMnN, 2% Si	закаляване	0,220	33,3	372
5	40Mn14Ni9Cr3AlV	зак.+ стареене +азотиране	0,142	3,87	815
6	X10CrNiTi 18 9	закаляване	0,340	64,2	246

Анализът на получените експериментални резултати на стойностите на износването и на коефициента на триене на стоманите в условията на абразивно износване показва, че комплексното легиране на хромманганови стомани с азот и силиций в количество съответно 1 и 3% (състави 1-3) осигурява по-високо съпротивление към износване в сравнение с азотираната стомана 40Mn14Ni9Cr3AlV. Стареенето на високоазотната хромманганова стомана, съдържаща ванадий (състав 1), допълнително повишава износоустойчивостта в сравнение със закаленото състояние.

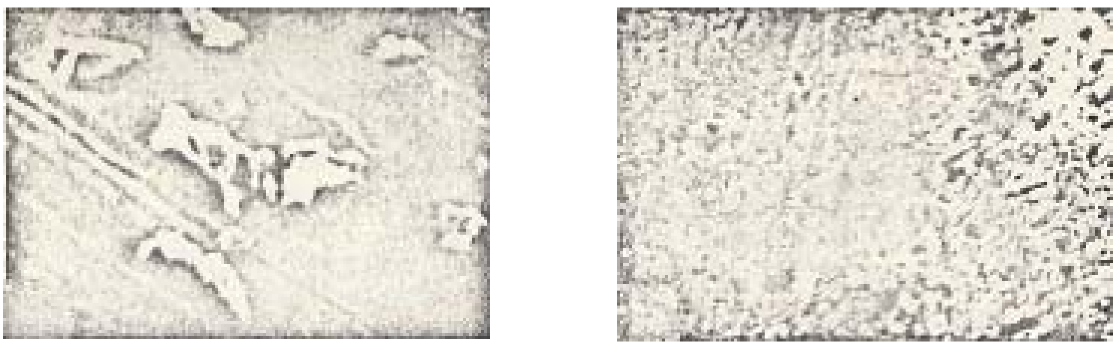
Установена е линейна зависимост на износоустойчивостта от натоварването и времето на изпитване (Фиг. 3). Скоростта на нарастване на износването след пришлайфане на контактните повърхности рязко намалява при увеличаване на съдържанието на N и Si в стоманата (състав 4). При съдържание в стоманата на 1% N и 3% Si (състави 1-3) скоростта остава почти постоянна.



а б

Фиг. 3. Зависимост на коефициента на триене fmp от натоварването P (kg) /a/ и на относителното износване (I=f_{mp}'- f_{mp}'', където f_{mp}' и f_{mp}'' – стойности на коефициента на триене съответно в края на изпитването и в края на пришлайфането) от времето на изпитване след пришлайфане /b/ при абразивно износване на изследваните стомани. Цифрите до линиите дават номера на съответния състав в таблицата

Съгласно [5] за много метални материали с хомогенна структура износването (*I*) на повърхността зависи от нейната твърдост (H_1), от твърдостта на контратялото (H_2) и е приблизително равно на *I* ≈ H_1-1,5 x H_2-1. Сравнението на получените по тази формула данни с експерименталните резултати показва, че експерименталното износване е малко по-голямо в сравнение с теоретичното. Тази разлика в износването е свързана със структурните особености на изследваните стомани и по-точно с особеностите на разпределението и с размера на частиците на уякчаващата фаза. При електронно-микроскопско изследване на образци след изпитване в условията на абразивно износване върху тяхната повърхност са установени ивици, широчината на които и разстоянията между тях зависят от нивото на износването. При по-малко износване е наблюдавано по-голямо разстояние между ивиците, образувани от абразивните частици (Фиг. 4)



а б

Фиг. 4. Микрофотографии (x1000) на повърхността на образците от хромманганови стомани: състав 4 /a/ и състав 3 /b/ след абразивно износване

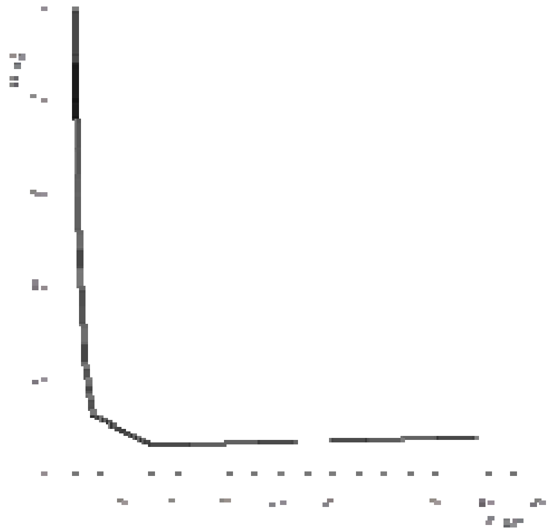
Това добре се съгласува с твърдостта на стоманите. Наличието в структурата на стоманите с високо съдържание на азот и силиций на голямо количество твърди (H≈1570 kg/mm^2) хромови нитриди от типа Cr_2N, равномерно разпределени в уякчената от азота аустенитна матрица, повишава нейното съпротивление към абразивно износване. В стоманата, съдържаща ванадий, допълнително уякчена от отделящите се при стареене дребнодисперсни ванадиеви нитриди

(H≈1520 kg/mm^2), този ефект се усилва, но неговото нарастване се определя от съотношението между размерите на отделящите се частици VN и на абразива (в дадения случай карбид от типа Me_3C с H≈840 kg/mm^2). Ако частиците на уякчаващата фаза са значително по-дребни в сравнение с частиците на абразива, то техният принос не е голям и зависи от величината на нарастване на якостта за сметка на дисперсионното твърдеене.

Изпитванията на високоазотните стомани, легирани със силиций, в условията на триене при търкаляне потвърдиха тяхната повишена износоустойчивост (Фиг. 5).

Сумарната загуба на тегло на ролки, изработени от аустенитни хромманганови стомани с 1% N, 3% Si, 1% V (състав 1), от азотираната аустенитна стомана 40Mn14Ni9Cr3AlV и от мартензитната стомана 38CrMoAl след изпитване при високи контактни напрежения до 80 kg/mm^2 е съответно 0,001; 0,02 и 0,018. Износоустойчивостта на високоазотните стомани е до 20 пъти по-висока в сравнение с предварително азотираната и безазотната аустенитна и мартензитна стомани. При изследване с помощта на растерен електронен микроскоп на повърхността на ролките след изпитване е наблюдавана гладка (без питингово разрушаване) повърхност. Послойното измерване на микротвърдостта на изпитаните ролки от високоазотната стомана (състави 1 и 3)- Фиг. 6, показва наличие на тънък (≈20 µm) повърхностен слой с висока микротвърдост (H≈600 kg/mm^2), съответстващ на ниското ниво на твърдост на работния азотиран слой на много стомани.

Фиг. 5. Зависимост на загубата на теглото (ΔP) от контактното напрежение (δ_{max}) при триене при търкаляне за стомани със състави 2, 3, 5 (цифри до линиите) и за стомана 38CrMoAl след азотиране (крива 7)



Фиг. 6. Изменение на микротвърдостта по сечението на образец от високоазотната стомана след изпитване на триене при търкаляне (δ_{max}=80 kg/mm^2; $\tau_{изп}$=240 h).

От концентрационните криви на разпределение на силиция и на азота, получени с помощта на рентгенов микроанализатор, не се установи обогатяване с тези елементи на зоната с повишена твърдост. Микроструктурният и рентгеноструркурният анализи показаха наличие в този повърхностен слой на дребнозърнеста ($d_{ср}$≈10 µm) аустенитна структура с голямо количество не много едри (<2 µm) нитриди. Съгласно данните от микрорентгеноспектралния анализ, в състава на нитридите освен хром и азот влизат силиций и въглерод. По този начин, липсата на деформационен мартензит и на сегрегация на легиращите елементи в слоя с повишена твърдост позволява получената износоустойчивост на високоазотните хромманганови стомани да се отнесе за сметка на деформационното уякчаване на аустенита с голямо количество нитридни частици. Незначителното увеличение на износването с нарастване на натоварването потвърждава казаното по-горе, тъй като високоазотните стомани се характеризират с бързо нарастване на плътността на дислокациите при пластичната деформация, осигуряващо непрекъснато поддържане на високо ниво на твърдостта на външния слой при запазване на пластичността във вътрешните обеми.

4. ЗАКЛЮЧЕНИЕ

Установено е повишаване на износоустойчивостта на изследваните високоазотни аустенитни стомани благодарение на значителното уякчаване на твърдите разтвори и на деформационното уякчаване, без образуване на деформационен мартензит. По стойностите на износоустойчивостта в условията на абразивно износване високоазотните (~1% N) хромманганови стомани, съдържащи силиций са на нивото на конвенционалните стомани. В условията на триене при търкаляне високоазотните хромманганови стомани съществено превъзхождат азотираната феромагнитна стомана 38CrMoAl и немагнитната стареещa стомана 40Mn14Ni9Cr3AlV.

ЛИТЕРАТУРА

25. LUKARSKI Y., P. TASHEV, CH. ARGIROV, H. KONDOV, Technological Solutions to Extend the Operating Cycle of Tools and Industrial Machinery. Transactions of Foundry Research Institute. Volume LVII. Year 2017. Number 4, pp. 253-258

26. RASHEV TS. High Nitrogen Steels. Metallurgy under Pressure. Academic Publishing House "Prof. M. Drinov". Sofia, 1995.

27. RASHEV TS. at all. Tool Steel Reference Book. Technika, 1990. (in bulgarian).

4.CH. ARGIROV, Y. LUKARSKI. Изследване на разтворимостта на азота във високоазотна неръждаема стомана от типа Cr20Mn15Mo2N1. Известия на НТСМ, 2016, Година XXIII, брой 1(187), pp. 126-129, ISSN 1310-3946.

5. ЯМПОЛСИЙ, Г. Я. и др. Исследование абразивного износа элементов пар трения качения. М. Наука, 1993, (in russian).

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Tribological Journal BULTRIB Vol. 7, 2018
Papers from the International Conference **BULTRIB'18**
25-27October 2018, Sofia, Bulgaria
Society of BulgarianTribologists
FIT – Technical University of Sofia

GRAPHENE - SOME BASIC ASPECTS

Juliana JAVOROVA, Svetla LEKOVA, Sandra SOVILJ-NIKIC, Virgil ILIUTA

Abstract: *The work aims at presenting the relatively new material graphene, which is of great interest due to the favorable combination of remarkable mechanical, thermal, chemical and electrical properties, as well as its expected wide application in the near future. Brief information on the history of its discovery, its structure and properties, some major applications to date, and expectations for future research are provided. Particular emphasis is also placed on the outstanding tribological characteristics of graphene, which increase its attractiveness for application in micro and nano devices and systems.*

Keywords: *graphene, carbon, 2D material, tribological characteristics*

1. INTRODUCTION

The paper aims at presenting the relatively new material graphene, which is of great interest due to the favorable combination of remarkable mechanical, thermal, chemical and electrical properties, as well as its expected wide application in the near future.

In recent years, a whole family of two-dimensional (2D) crystalline materials have been identified and analyzed. As their representative, graphene is the world's first 2D material to represent a single layer of carbon atoms. Due to its enviable properties, since its isolation it has captured the attention of scientists, researchers and industry around the world.

The paper gives in synthesized form brief information about the history of its discovery, structure and its properties, some major applications at the time, and expectations for its future use and new research.

Furthermore, its exceptional tribological characteristics are emphasized. Due to its superior strength, graphene has great potential to be used as an ultra-thin protective coating for various precision components. It turns out that various graphene coatings can be successfully used to reduce friction and wear in nano-, micro- and macro-mechanical applications. However, the conditions under which graphene serves as an effective protective coating remain a function of the operating parameters.

2. HISTORY

Theoretically, the graphene has been studied by P. R. Wallace as early as 1947 as a starting point for exploring the electrionic propertiesof 3D graphite.

However, for the first time, graphene is isolated in 2003 at the University of Manchester by both Russian researchers Prof. Andre Geim and Prof. Konstantin Novoselov.

The method of isolation used is somewhat rudimentary: Using a sticky tape strip, both scientists remove from the lump of graphite thin flakes, which transfer to a silicon substrate, noting that some of the flakes are thinner than others (Fig. 1). By separating the graphite fragments sequentially and repeatedly, they manage to separate flakes with a thickness of only one atom [1]. Their experiment leads to the isolation of graphene for the first time.

Fig. 1. Atomic Force Microscopy (AFM) picture of a monolayer of graphene, [1] (the black area is the silicon substrate, the dark orange is a mono layer of graphene with thickness of~ 0.5 nm, the bright orange part contains a few layers with thickness of~ 2 nm)

The discovery is so bizarre that at the beginning even encounter skepticism from the scientific community [2]. The journal Nature even rejected twice their article about the experiment and results. Ultimately their research with the description of the preparation, isolation, identification and characteristics of graphene were published in 2004 in the journal Science [3]. Six years later, in 2010 Geim and Novoselov win Nobel Prize in Physics for their discovery [4].

3. STRUCTURE, PROPERTIES, FORMS

3.1. Structure and properties

Graphene is a unique material that should be considered as composed of sp^2-bonded carbon atoms, which form a stable, self-retaining sheet with a thickness of only one atom.

In other words, graphene is a single layer (flat sheet) of carbon atoms, forming a finite number of hexagonal lattices, similarly to a flat honeycomb [5], but that is a million times thinner than a sheat of paper (Fig. 2). In turn, the graphite, the most common type of carbon in the form of lead pencils, has substantially a structure consisting of multiple layers of graphene stacked one above the other. In fact, one millimeter of graphite consists of three million layers of graphene stacked on top of one another.

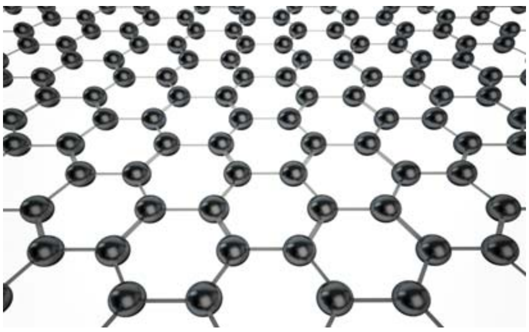

Fig. 2. Graphene atoms are arranged in hexagonal lattices

Namely the already described arrangement of the graphene atoms predetermined its enviable electrical and mechanical properties (strength) and good electrical and thermal conductivity, which are higher than those of copper. Due to its two-dimensional structure (which is maintained even at room temperature), it is extremely thin and flexible, which, along with its other properties, makes it a unique material that can be used in aviation, automotive, electronics, battery manufacturing and many more. Its field of action can be greatly expanded, as graphene can be combined with other elements and then the resulting substances with each other.

Graphene is called "material-miracle" because of its superior properties and the scientists are still looking for various potential applications. It is thin and flexible but stronger than diamond and it is, in fact, the strongest material ever tested, with an intrinsic tensile strength of 130 GPa and a Young's modulus of 1 TPa [5]. Graphene is very light and weighs only 0.77 mg/m^2. At the same time it is transparent, highly electrically and thermally conductive and impermeable to most gases and liquids [1, 5, 2].

All these unique properties of graphene lead to the rapid disclosure of its potential applications shortly after its isolation.

3.2. Forms of the graphene

It is known that carbon can exist in several different allotropic forms.

The most common form is graphite, which is composed of hexagonal carbon sheets (layers), which are glued on each other [1, 6]. Diamond is the most stable form of carbon and is formed under high pressure.

With their discovery, Geim and Novoselov show that from graphite can be isolated a single carbon sheet, as it remains stable in an isolated state. The single carbon sheet is called graphene (Fig. 3).

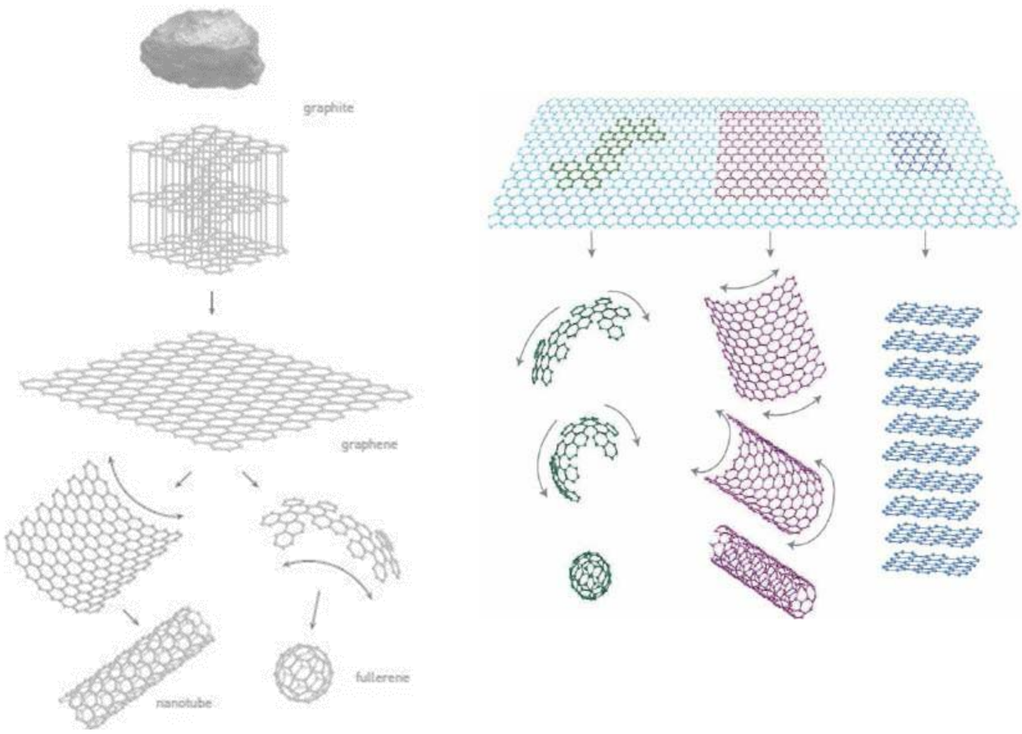

Fig. 3. Two different schemes for presenting the forms of graphene - graphite, fullerenes, carbon nanotubes

Fullerenes are a new form of molecular carbon [1, 6]. Generally speaking, they contain 60 carbon atoms and looks like a soccer ball, formed by 20 hexagonal and 12 pentagonal structures. This is what allows them to form a sphere.

Closest to fullerenes quasi-one-dimensional forms of carbon - the carbon nanotubes [1, 6] have been known for several decades but monoatomic nanotubes are known since 1993. They can be formed from graphene sheets that are rolled into a tube and their ends are hemispherical, like fullerenes.

Graphene-like structures have been known since the 60's of the 20th century, but as mentioned above, at this time there are still experimental difficulties in isolating single carbon sheets [1, 6].

4. APPLICATIONS AND FUTURE RESEARCH

Due to its numerous positive characteristics, graphene has been the subject of intensive research for potential applications. Remarkable in so many ways, graphene inspires scientists to think of a wide range of applications in various fields (Fig. 4), such as consumer technology and environmental science.

If that material goes into mass production, flexible devices, superfast quantum computers, electronic clothing as well as devices that can communicate with cells in the human body may soon be expected.

Scientists at the University of Manchester [7] state that, in addition to its powerful electrical properties, graphene is of the few materials in the world, that are simultaneously transparent, flexible and good conductors, and together these properties are extremely rare in one and the same material.

This makes it ideal for use in portable electronic devices. With the application of graphene-technologies smartphones and tablets could become much more durable, thinner, faster and cheaper than silicon-based ones. It will be able to create extremely compact touchscreens and smartphones that have the thickness of a sheet of paper and can be folded to make it more convenient carrying them in the pocket [8]. Samsung has already begun production of flexible displays and next-generation devices. The latter are already a fact from last year, but according to some information references the graphene-technologies are not fully integrated into these products. With graphene these devices can be made even more useful, designed to fit snugly around the limbs and to bend when necessary. Of course, Samsung is not the only company looking for ways to use the wonder material. Researchers from IBM, Nokia, SanDisk, etc. have been experimenting with graphene for a long time trying to create miniature sensors, transistors and Solid State Drive memories.

However, the flexibility and microscopic width of graphene also provide useful opportunities in biomedical research. Miniature sensors and devices can be created with material graphene, capable of moving easily and harmlessly through the human body, analyzing tissues, or even delivering drugs to specific areas.

Graphene is both highly conductive and transparent. As such, it has great potential as a material in solar panels and solar cells.

Usually, solar cells use silicon, but they provide approximately 25% efficiency in the conversion of solar energy, which is significantly less than the estimated 60% efficiency of graphene solar cells [2]. Although to the current time studies in this area are still theoretical, studies of graphene solar cells are continuing and their effectiveness is increasing.

Because of its high conductivity, graphene can be used in semiconductors to significantly increase the speed of information transmittion.

Recent tests have shown that semiconductor polymers conduct electricity much faster when placed on a graphene layer than on a layer of silicon, and this applies even with a thicker polymer layer.

The tight atomic bonds of graphene make it impermeable to almost all gases and liquids with water being the exception. Since water can be evaporated by graphene while most other gases and liquids cannot, graphene can be an exceptional filtration tool [2].

Graphene can be especially useful for purifying water from toxins. There have been published studies, which showed that oxidized graphene can even retrieve radioactive materials such as uranium and plutonium present in water, leaving the liquid free of contaminants. Furthermore, thanks of graphene it could be possible to clean nuclear waste and chemical runoff, considered as some of the biggest environmental hazards to the current time.

It is well known that overpopulation continues to be one of the most pressing environmental problems in the world. In that relation, providing drinking water will become increasingly important. Graphene filters (with dozens of times less energy requirements than reverse osmosis ones for filtering the seawater) have a huge potential to improve water purification and by this way to increase the amount of fresh water available.

Fig. 4. Applications of graphene

Graphene is 100% resistant to all acids and corrosion. Graphene based paint has already been developed that can practically be considered eternal.

A battery for cell phones based on graphene and silicon has been created in the United States, lasting up to a week with a single charge, while the latter lasts only 10 minutes. China has already produced graphene batteries for smartphones that charge up to 80% of their capacity in a minute. This type of battery is expected to charge electric vehicles in just a few minutes.

Other potential applications of graphene include new ultra-strong composite materials that are incredibly thin, elastic and lightweight used in satellites, aircraft, automotive, and many more.

5. SOME TRIBOLOGICAL ASPECTS

Exceptional mechanical properties, high chemical stability and a very low coefficient of friction of graphene predetermine its treatment as a promising 2D solid lubricant, as well as the thinnest antiwear and corrosion-resistant coating.

In that relation, miniaturized devices with high surface/volume ratios, such as micro- and nanoelectromechanical systems, are a suitable object of future tribological application of graphene. Moreover, thanks to its excellent strength characteristics [9], graphene has great potential for use as an ultra-thin protective coating for various precision components exposed to contact stress.

The various graphene coatings, graphene as a lubricant and as a reinforcing material in a metal matrix can be successfully used to reduce friction and wear in a wide variety of other tribological applications. In this regard, numerous studies are being conducted around the world.

Some reaserch related to applying graphene protective coatings as a nanoscale solid lubricant have been described in the review papers [9, 10]. Graphene is primarily considered as a nanomaterial and, in this regard, research is predominantly devoted to the tribology of graphene at the nano level (Fig. 5). AFM is the most commonly used tool for conducting such kind of research (Fig. 6).

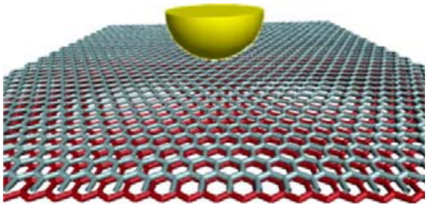

Fig. 5. Simulation of a spherical nanoasperity sliding over a graphene film (gray bonds) supported by a substrate of rigid atoms (red bonds)

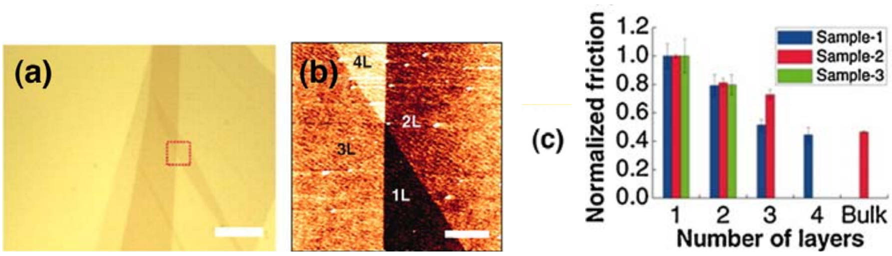

Fig. 6. (a) Bright-field optical microscope image of graphene sample; (b) Topographic and friction (forward scan) images measured simultaneously by AFM; (c) Friction on areas with different layer thicknesses, [10]

As one of the first tribological studies on graphene could be mention the work of Lee et al. [11], where is given an experimental determination of the friction forces and the coefficient of friction for graphene and graphite. Experiments show that the behavior of graphene and graphite is quite different, although these materials have a similar surface in terms of morphology and chemical structure.

On the other hand, the tribological characteristics of graphene coatings depend on the adhesion between the coating and the particular substrate [12]. The coefficient of friction is influenced by different parameters, as well as by the material on the original substrate, such as the coatings on nickel have a lower coefficient than the coatings on copper (Fig. 7). The characteristic parameters of the friction and wear of the multilayer graphene are improved when graphene is tightly bonded to the particular substrate and shows nanoscale changes in thickness. At the same time, for multilayer graphene, AFM studies have confirmed that as the number of graphene layers increases, the friction is reduced (Fig. 8).

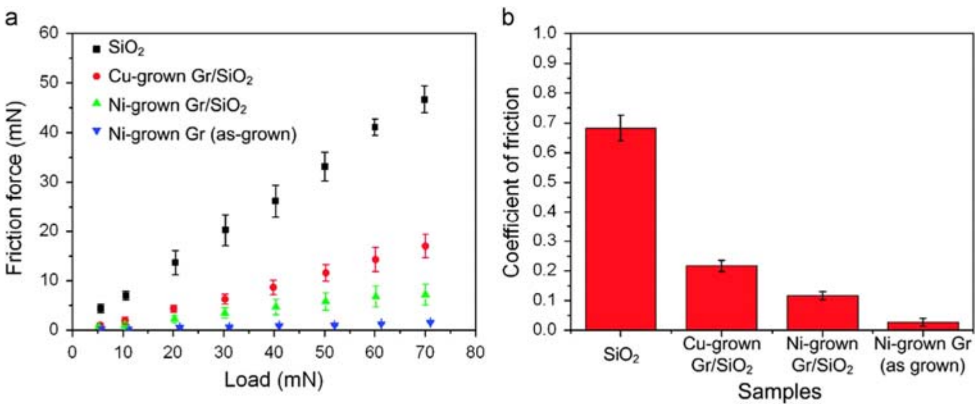

Fig. 7. (a) Friction force as a function of load and (b) coefficient of friction for graphene samples. /Gr- graphene/, [12]

Tribological research in microscale show that the introduction of defects in the graphene increases friction [13]. Tribological studies of graphene as a lubricant additive clearly confirm that it reduces friction and wear regardless of weather conditions (wet or dry) and also acts as a perfect passivation layer. Macroscale studies show that graphene layers largely suppress the friction and wear of sliding interfaces.

Decreasing sliding friction of steel on steel with the addition of graphene flakes as a solid lubricant [10] is explained by the low shear and the highly protective nature of graphene resulting from its ability to increase the surface load capacity [13]. Moreover, when graphene is defected, it loses its ability to provide less friction and wear.

The literature review shows that the graphene has already been used for improving the tribological performance of the nano, micro and macro level in a variety of applications at room temperature. Extensive research is needed on the use of graphene and for applications at high temperatures such as those in the space industry, internal combustion engines, etc. [14].

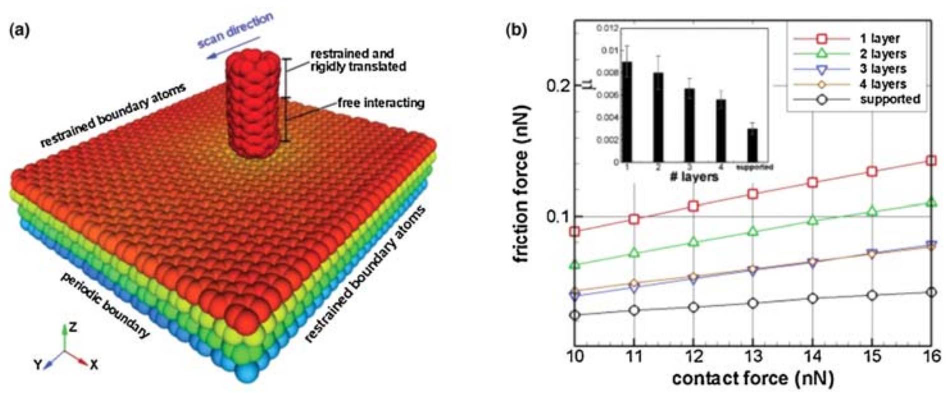

Fig. 8. (a) Four-layer suspended graphene assembly. (b) Contact force vs. Friction force and the corresponding friction coefficients as function of number of layers, [10]

Together with other remarkable characteristics of the graphene, it is non-toxic and environmentally friendly. In addition to using graphene as a surface coating or solid lubricants, graphene sheets are also considered as 'green' lubricant additives since graphene contains the elements C, H and O instead of N, S, P and heavy metals. Furthermore, graphene has no toxic particles.

The tribological properties of graphene oxide nanosheets in mineral oil have also been investigated under boundary and mixed friction and under elastohydrodynamic conditions [15]. The experiments concern to the monitoring of the reduction of friction due to the addition of nanosheets dispersed in oil. The results clearly demonstrate that the lubricant based on graphene platelets forms a protective film, thus preventing direct contact between the steel surfaces and improving the lubrication of the base oil. In testing the graphene as a lubricating additive in greases [16], it was found that as compared with the graphite, the multilayered graphene as an additive for bentonite lubricating grease reduces the friction and wear, but also significantly improves the thermal stability and load capacity of lubricating grease.

As mentioned above, graphene is gaining interest as a unique and attractive material that is used in many applications such as electronics, mechanical and tribological systems. Despite the ultra-thin nature of graphene sheets, they are effective in reducing friction and wear, not only at contact loads on a microscale, but also at relatively high loads with and without lubricant and also partially under high temperature conditions. It has been found that graphene is effective even on metal substrates, with typical surface topography [14]. Using graphene as a lubricating additive and as a reinforcing material the graphene nanoparticles contribute directly to the formation of tribologicalfilm which helps to reduce the coefficient of friction.

Recent studies in the field of biosurface engineering (engineering surfaces for biomaterials) show that graphene-based materials combine their excellent mechanical and tribological properties with good biocompatibility and attractive antibacterial properties [17]. Therefore, graphene-based materials can also potentially be used for engineering surfaces of biomaterials for high-performance, long-lasting medical devices and body implants (Fig. 9).

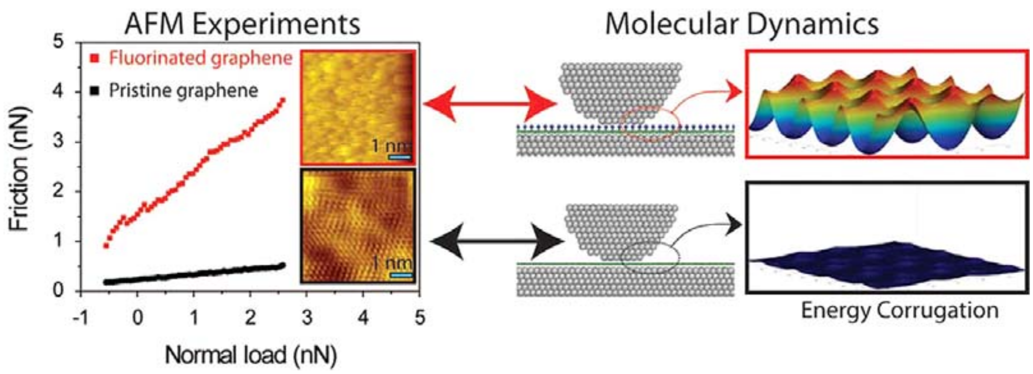

Fig. 9.Tribological study of graphene in the field of biosurface engineering, [17]

With the growth of more economical methods for the synthesis of graphene, its use in tribological applications is expected to increase steadily in the near future.

6. CONCLUSION

It is no coincidence that scientists claim that graphene has the potential to change our world fundamentally.

Despite the long list of strengths of graphene, it is still not widely used. One of the main factors is its high cost of production in large quantities, which limits its use in products requiring mass production. So, as always the economiccal aspects influence significantly. Furthermore, when creating large graphene sheets, there is an increased risk of small cracks and other material defects.

Research on graphene continues to be active despite mass production problems. Research institutes of the University of Manchester, where graphene was first discovered are continually filing patents for new methods relating to graphene - for its obtaining and applications. The same situation is also observed in many research laboratories around the world. It is known that in few years ago the EU approved the funding of one of its flagship programs specifically to support graphene research in the field of electronics. As already noted, many major technology companies in Asia (including Samsung, HTC, Huawei, etc.) are conducting intensive research on graphene. As the EU seeks to strengthen its position in the face of Asia's explosive economic growth, graphene may be an important battleground for international politics in the coming years [2].

The existence of limitations in the use of graphene does not currently prevent research teams from seeking new applications, from light bulbs to body armor [5].

Obviously not all related to our expectations of graphene will be happen as soon as we want. It is known that [2], the silicon was discovered in the mid-19th century, but it took nearly a century before silicon semiconductors paved the way for the rise of computers. Whether graphene with its almost mythical qualities can be the resource that would propel the next leap in our scientific and technological development? Really only time will tell.

ACKNOWLEDGEMENTS

The present work involves performing of tasks under CEEPUS Network CIII-BG-0703-07-1819. The authors are very grateful to the CEEPUS Program as well as to RDS at UCTM Sofia for the support of this study.

REFERENCES

1. Scientifc Background on the Nobel Prize in Physics 2010 - Graphene, Royal Swedish Academy of Sciences, 2010.
2. Nicol W., What is graphene, Digital trends, Emerging Tech, 2018.
3. Novoselov K.S., Geim A.K., Morozov S. V., Jiang D., Zhang Y., Dubonos S. V., Grigorieva I.V, Frisov A.A., Electric Field Effect in Atomically Thin Carbon Films, Science, 2004, 306, 666-669.
4. The 2010 Nobel Prize in Physics - Press release, Royal Swedish Academy of Sciences, 2010.
5. Graphene - The Carbon-Based 'Wonder Material', Compound Interest, 2015.
6. Sachanska G., The 2010 Nobel Prize in Physics – Graphene, Summary of the official Nobel Foundation material, DMBSci NBU Annals, 2011, Vol. 7.
7. https://www.graphene.manchester.ac.uk/learn/graphene-and-2d-materials/
8. Popov D., Why the future belongs to graphene?, Investor.bg, 2014.
9. Penkov O., Kim H. J., Kim H. J., Kim D. E. (2014). Tribology of graphene: a review. International journal of precision engineering and manufacturing, 15, 3, 577-585.
10. Berman D., Erdemir A., Sumant A. V., Graphene: a new emerging lubricant. Materials Today, 2014, 17, 1, 31-42.
11. Lee H., Lee N., Seo Y., Eom J.,Lee S. Comparison of frictional forces on graphene and graphite. Nanotechnology, 2009, 20, 32, 325701.
12. Kim K. S. et al., Chemical vapor deposition-grown graphene: the thinnest solid lubricant, 2011, ACS Nano, 5, 6, 5107-5114.
13. Klemenz A. et al., Atomic Scale Mechanisms of Friction Reduction and Wear Protection by Graphene, Nano Letters, 2014, 14, 12, 7145-7152.
14. Kumar P, Wani M., Synthesis and tribological properties of graphene - A review, Jurnal Tribologi, 2017, 3, 36-71.
15. Senatore A. Et al., Graphene oxide nanosheets as effective friction modifier for oil lubricant: materials, methods, and tribological results. ISRN Tribology, 2013.
16. Fan X., Xia Y., Wang L., Li W, Multilayer graphene as a lubricating additive in bentone grease. Tribology Letters, 2014, 55(3), 455-464.
17. Dong H, Qi S., Realising the potential of graphene-based materials for biosurfaces – A future perspective, Biosurface and biotribology, 2015, 1, 229-248.

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Tribological Journal BULTRIB Vol. 7, 2018
Papers from the International Conference **BULTRIB '18**
25-27 October 2018, Sofia, Bulgaria
Society of Bulgarian Tribologists
FIT – Technical University of Sofia

ТРИМЕРНО БИОПРИНТИРАНЕ ЗА ТЪКАННОТО ИНЖЕНЕРСТВО

Юлияна ЯВОРОВА

Абстракт: *Работата представя накратко същноста на тримерното биопринтиране на човешки тъкани. Дадена е информация за етапите на основния процес, прилаганите методи и материали за тази сравнително нова технология. Описани са някои успешни приложения на 3Д биопечата и са маркирани очаквания за неговото бъдещо развитие. Показана е значимоста на биопринтирането като стимул за нова индустриална конвергенция на медици и инженери от различни направления.*

Ключови думи: *тримерно биопринтиране, биоматериали, тъканно инженерство*

1. ВЪВЕДЕНИЕ

Биопринтингът (печат на биологични структури като тъкани и органи за трансплантация) е нова област на изследване и техника, която включва принтиращи устройства, които влагат биологичен материал. Дългосрочна цел е технологията да бъде използвана за създаване на тъкани и органи или дори цели органови системи от живи биологични материали.

Тримерният печат за получаване на клетъчни конструкции е представен за първи път през 2003 г. от Thomas Boland от Clemson University, патентовал използването на мастиленоструен печат за клетки [1, 2]. Биопринтингът се разглежда като потенциално решение за глобалния недостиг на донорни органи. Органите, които са били успешно отпечатани и приложени в клинична обстановка са плоски (напр. кожа), съдови (напр. кръвоносни съдове), или кухи (напр. пикочен мехур).

Фиг. 1. Компоненти на биопринтирането

Тримерното (3D) биопринтиране се нарича процесът по създаване на клетъчни щампи в определено ограничено пространство, използвайки технологиите за тримерен печат, като клетъчните функции и жизнеспособност биват запазени в принтирания продукт (Фиг. 1). 3D биопринтирането използва най-вече метода с послойно нанасяне на материали, известни като биомастила, с цел създаване на подобни на тъкан структури, които да се използват за нуждите на медицината и тъканното инженерство. В сравнение с небиологичния печат, при 3D биопечатът се включват усложняващи фактори като избор на материали, типове клетки, фактори на растежа и диференциацията, както и допълнителни технически предизвикателства, свързани с чувствителността на живите клетки и изграждането на тъканите.

Цел на настоящата работа е да представи едно кратко обобщение на процеса, използвани методи, материали и някои приложения на тримерното биопринтиране.

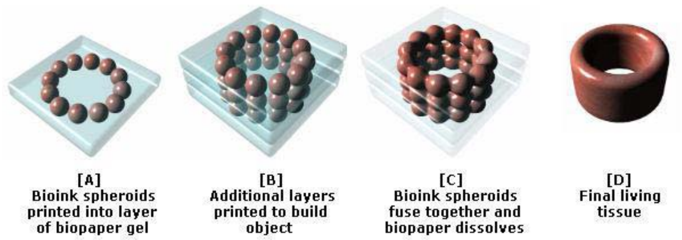
2. МАТЕРИАЛИ

2.1. Видове

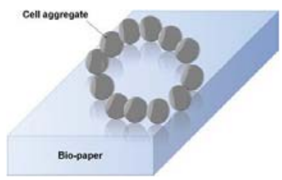
Материалите за 3D печат обикновено се състоят от алгинатни или фибринови полимери, интегрирани с клетъчни адхезионни молекули, които поддържат физическото прикрепване на клетките [3]. Такива полимери са специално проектирани да поддържат структурната стабилност и да възприемат клетъчната интеграция.

Хидрогелните алгинати са едни от най-често използваните материали при биопринтиране, тъй като те са много адаптивни и могат да бъдат фино настроени, за да симулират определени механични и биологични свойства, характерни за естествената тъкан. Способността на хидрогелите да бъдат съобразени с конкретните нужди позволява да се използват като адаптивно скеле, което е подходящо за различни тъканни или органични структури и физиологични условия [4].

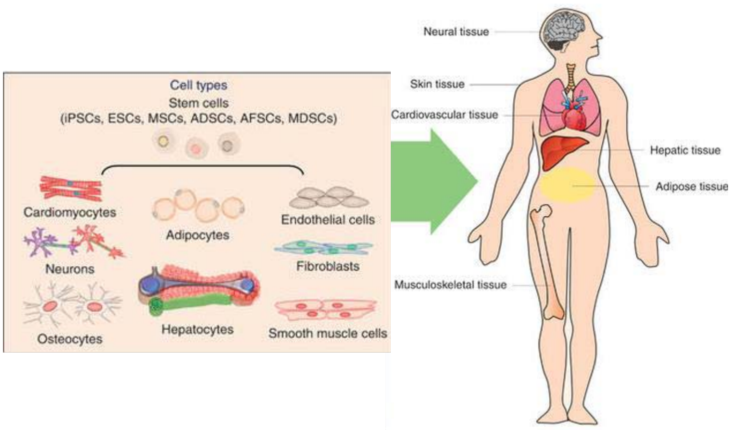
Най-общо казано основните материали за биопринтирането са биомастила (клетки взети от биопсия или стволови клетки) и биохартия (хидрогел, колагени, нутриенти и др.).
Някои схемни решения за тези материали и тяхното интегриране в цялостния процес на биопечатането са представени по-долу (от Фиг. 2 до Фиг. 6).



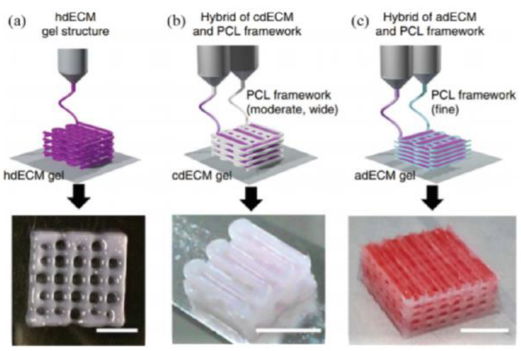
Фиг. 2. Клетки от биомастило върху слой от хидрогел



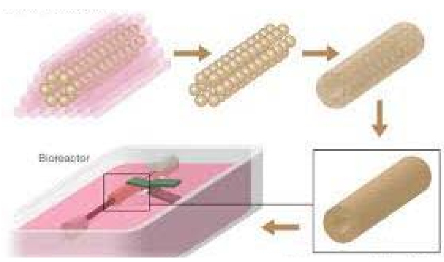
Фиг. 3. Клетъчен агрегат върху биохартия



Фиг. 4. Типове клетки в различни видове тъкани на човешкото тяло



Фиг. 5. Принтиране на хидрогел като скеле/матрица на бъдещата тъкан



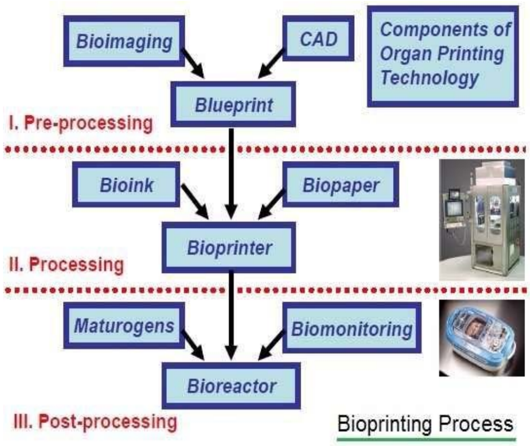
Фиг. 6. Биоматериали в процеса на биопечат

2.2. Необходими свойства на материалите за биопечат

Успешното прилагане на материалите, използвани за биопечат (биомастила и биохартия), предполага те да притежават следните свойства [5]: годност за печат; биосъвместимост; кинетика на разграждане и нетоксичност на вторичните продукти при разграждане; добри физико-механични свойства; биомимикрия на биоматериалите.

3. ПРОЦЕС

Цялостният процес на 3D биопринтирането протича най-общо казано в следните три етапа [6, 7]: предбиопечат, биопечат и постбиопечат (Фиг. 7).



Фиг. 7. Компоненти на технологията за принтиране на тъкани и органи

3.1. Предбиопечат (pre-bioprinting; pre-processing)

Предбиопечатът е процес на генериране на компютърен модел, който впоследствие ще бъде създаден от биопринтера, както и съответния избор на материали, които ще бъдат използвани за тази цел.

Като задължителен етап в началото трябва да бъде получено точно дигитално изображение на съответната тъкан или орган посредством съвременните методи и технологии за образна диагностика – компютърна томография (КТ) и ядрено-магните резонанс (ЯМР). Впоследствие се прави томографска реконструкция на изображенията, които сведени до двумерни проекции (CAD) се изпращат на биопринтера за съответното послойно отпечатване.

След като образът бъде създаден посредством КТ и/или ЯМР [5], определени клетки от тъканта (взети чрез биопсия или стволови клетки) се изолират и подлагат на размножаване. Впоследствие тези клетки се смесват със специален втечнен материал, който осигурява кислород и хранителни вещества, които поддържат виталитета на клетките.

3.2. Биопечат (bioprinting; processing)

На следващия етап „биомастилото“ от клетки, междуклетъчно вещество и хранителни вещества се поставя в съответната касета на биопринтера. При биопечата биомастилото се отлага в съответствие с медицински сканирани изображения на пациента. Когато биопринтираната ‘пред-тъкан’ бъде преместена в т.нар. инкубатори, тя се развива до тъкан. 3D биопечатане за изработване на биологични структурни елементи (тъкани/органи) най-често се базира на впръскването на биомастилото (клетки) върху биосъвместимо скеле (биохартия), използвайки последователен послоен подход, за да се генерират тъканоподобни тримерни структури. Важно е да се отбележи, че получените с 3D биопринтиране изкуствени органи като напр. черен дроб и бъбреци нямат жизненоважни компоненти като кръвоносни съдове и др., без които е невъзможно осигуряване на клетъчната жизнеспособност и стабилност по време на процеса на създаване на тези биопринтирани органи [8].

3.3. Постбиопечат (post-bioprinting; post-processing)

Третият основен етап – постбиопечат се осъществява в биореактори и осигурява създаването на стабилна структура от изпринтирания биологичен материал. Този процес гарантира съхранявнето на механичната цялост и функционалност на отпечатания с тримерно принтиране обект посредством механични и химически стимулации. Тези стимулации представляват изпращане на сигнали на клетките за контролиране на ремоделирането и растежа на тъканите. В биореакторите се осигурява и бързото съзряване на тъканите и сдобиването им с кръвоносна система (васкуларизация), както и способността им да толерират трансплантирани тъкани [7].

Друго основно предназначение на биореакторите е да способстват за преноса на хранителни вещества до тъканите, създаване на подходящи микрогравитационни среди и др. Различните видове биореактори са подходящи за различни видове тъкани, например генерирането на хрущялна тъкан е подходящо да се осъществява в биореактори с компресия.

4. ПОДХОДИ

Тримерното биопринтиране се основава на следните три основни метода, наричани още подходи за възпроизвеждане на живи биологични тъкани [5]: биомимикрия, автономно самоасемблиране и изграждане на мини-тъкани (Фиг. 8).

Фиг. 8. Основни методи/подходи за 3D за биопечат

4.1. Биомимикрия

Биомимикрията представлява създаване на подредени структури, идентични с естествените такива, които се намират в тъканите и органите на човешкото тяло [9]. Тя включва производството на идентични репродукции на клетъчните и извънклетъчните компоненти на тъкани или органи.

4.2. Автономно самоасемблиране

Друг подход към възпроизвеждането на биологични тъкани е да се използва развитието на ембрионалните органи като основен метод [5]. Този подход се основава на физическия процес на развитие на ембрионалните органи като модел за възпроизвеждане на съответната тъкан.

Схемата "без скеле" на този подход използва самосглобяеми клетъчни сфероиди, които се подлагат на сливане и клетъчна организация, за да имитират развиващите се тъкани. Автономното самоасемблиране се основава на клетката като основен двигател на хистогенезата, насочвайки състава, локализацията, функционалните и структурните свойства на тъканта.

4.3. Мини-тъкани

Те могат да бъдат определени като най-малкия структурен и функционален компонент на тъканта [5]. Мини-тъканите могат да бъдат създадени и сглобени в по-голямата конструкция (функционален макротип, наречен макро-тъкан) чрез рационален дизайн, самоасемблиране или комбинация от двете.

5. АПАРАТУРА И СОФТУЕР

5.1. Апаратура

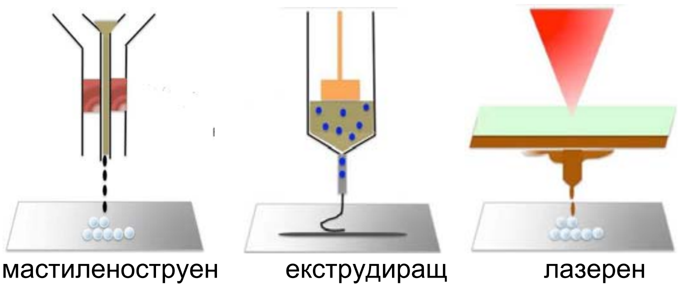
В сравнение с обикновените мастилени принтери, биопринтерите (Фиг. 9 и Фиг. 10) имат три основни компонента. Това са използвания хардуер, вида биомастило и материала, върху който се отпечатва (биоматериал) [6].

Фиг. 9. 3D Discovery Evolution биопринтер

Фиг. 10. 3D биопринтер на бъдещето

Както вече бе споменато, биомастилото е материал, произведен от живи клетки, който има поведение на течност, позволявайки да бъде "отпечатан" и с възможност за създаване на желана форма. За да бъде получено биомастилото се създава суспензия от клетки, разположена в хранителна среда. Биомастилото се зарежда в патрон/касета и се поставя в биопринтера, заедно с друга касета, съдържаща гел (хидрогел), известен като биохартия [10].

Може да се обобщи, че биопринтерът включва две печатащи глави, едната за поставяне на човешките клетки, а другата за поставяне на хидрогел, скеле или поддържаща матрица. Клетките, които се използват от устройството трябва да бъдат клетки на тази тъкан (или орган), която ще се възстановява – напр. изграждането на артерия изисква артериална клетка [11].



Фиг. 11. Видове биопринтери

При биопринтирането се използват три основни типа принтери (базирани на трите различни метода на биопринтиране). Това са мастиленоструйни, лазерни и екструдиращи принтери (Фиг. 11).

Мастиленоструйните принтери се използват предимно за биопечат на „широкомащабни” (по-големи) продукти. Бъдещата тенденция при тях е отпечатване на материали в точни количества, което минимизира разходите и отпадъците [12]. Един общ недостатък на този тип биопринтиране е, че биологичният материал трябва да бъде в течна форма, за да позволи образуването на капчици; като резултат, отпечатаната течност трябва след това да формира солидна 3D структура с подходяща организация и функционалност. Друго ограничение при тях е трудност при постигането на биологично значими клетъчни плътности. От друга страна, мастиленоструйните биопринтери притежават и няколко съществени предимства, включително ниска цена, висока разделителна способност, висока скорост и съвместимост с много биологични материали. Лазерните принтерите осигуряват печат с висока резолюция, но тези принтери често са много скъпи. Екструдиращите принтери отпечатват клетките слой по слой, точно както 3D принтирането за създаване на 3D изделия. В допълнение към самите клетки екструдерите могат да използват и хидрогелове, които се вливат заедно с клетките [6]. Основното предимство на технологията за биопечат с микроекструдиране е способност за отлагане на много високи клетъчни плътности.

5.2. Софтуер

3D биопринтерът включва софтуерен интерфейс, който позволява изграждане на модел на тъканната конструкция преди принтера да започне да конструира органите клетка по клетка и за целта използва автоматизирани лазерно–калибрирани печатни глави. Едни от масово използваните софтуерни продукти [13] към момента са:BioCAD, BioCAM, BioCUT и др. (Фиг. 12).

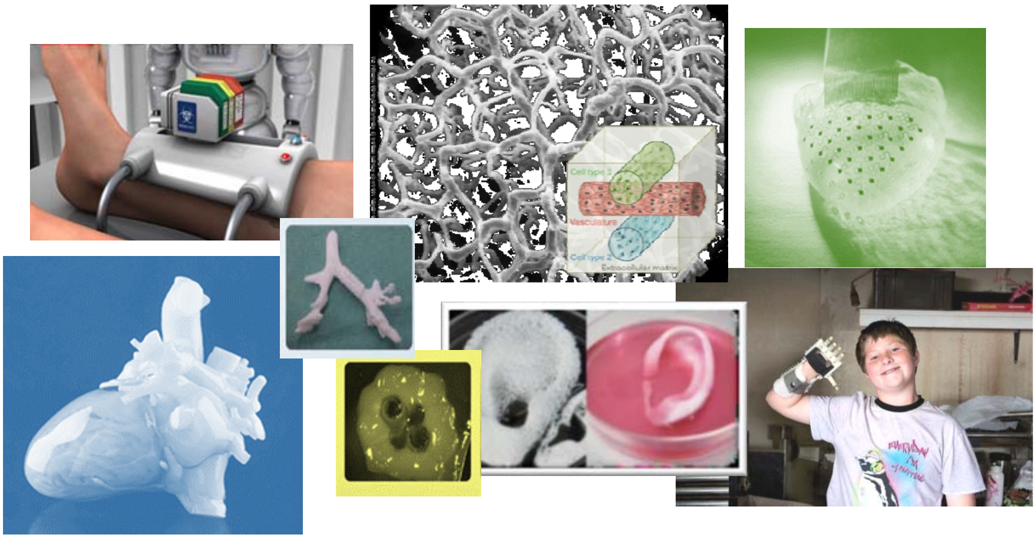
Фиг. 12. Интерфейс на софтуерни продукти за 3D биопринтиране

6. ПРИЛОЖЕНИЯ

Биопринтирането е съвременна мощна технология за производството на тъкани и органи, която колаборирайки си с медицината, биотехнологиите, фармацевтиката и инженерните науки ще има все по-голямо значение за здравеопазването на човечеството в недалечно бъдеще.

Тъй като биопринтерите имат своето конкретно медицинско приложение, възпроизвежданите ‘изкуствени’ органи ще бъдат съобразени изцяло с индивидуалните особености на пациента. Всеки биоразпечатан ‘артикул’ ще бъде създаден от култура от собствени клетки на пациента и по този начин рискът от отхвърляне на съответния орган за трансплантация ще бъде сведен до минимум.

Потенциалът на тази нова технология може да се покаже със следните успешни примери (Фиг. 13) на тримерно принтиране:



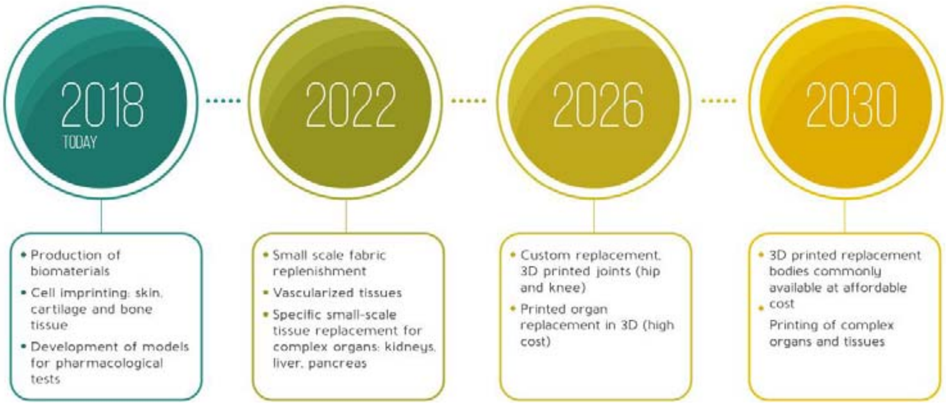
Фиг.13. Конкретни приложения на биопринтирането

- Тъкани с кръвоносни съдове - кожни клетки, преплитащи се в съединителната тъкан, които потенциално могат да функционират като кръвоносни съдове (Harvard, MA, USA);
- Протези – създаване на сравнително евтини и лесно приспособими протезни части за пациенти (Toronto, CA);

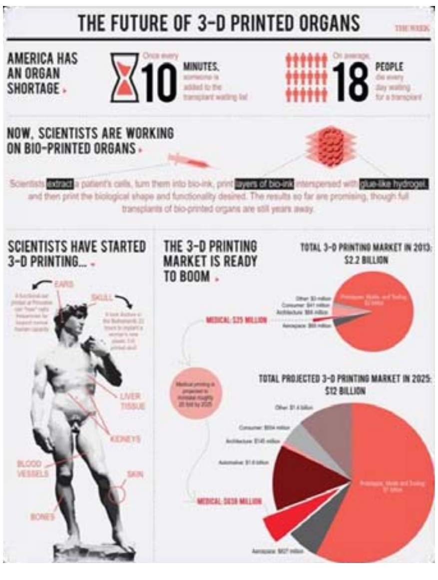
- Изпитване на лекарства – върху прототипи на живи тъкани и органи, получени посредством биопринтиране (Glasgow, UK);
- Сензори за човешки органи – отчитане на промени в температура, налягане, обеми, киселинност на средата (St. Louis, MI, USA);
- Медицински модели – за изследване на растеж и разпространение на тумори (USA, China);
- Отпечатване на органи - сърдечна клапа, ухо, кожа.

7. БЪДЕЩЕ

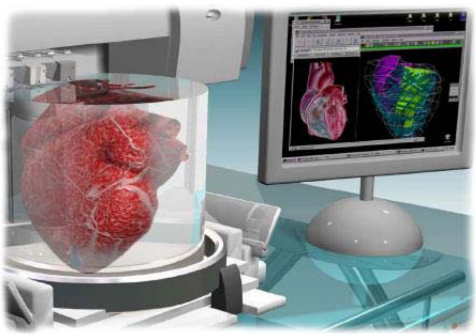
Заедно с напредъка в областа на нанотехнологиите и генното инженерство биопринтирането може да се окаже мощен инструмент за тези, които се стремят към удължаване на живота [14]. Наред с това, принципите и технологията на биопринтирането неизбежно ще стимулират и по-нататъшната нова индустриална конвергенция, като лекари, инженери и компютърни специалисти все повече ще овладяват знанията и уменията за манипулиране на живата биотъкан още на най-базово клетъчно ниво.



Фиг. 14. Очаквано развитие на 3D биопринтирането в следващото десетилетие



Фиг. 15. Бъдещето на 3D биопринтирани органи



Фиг. 16. Биопринтиране на сърце

Проучването на специализираната литература показва, че към момента вече са факт: производството на биосъвместими биоматериали, отпечатване на кожна тъкан, хрущяли и малки ставни тъкани. До три-четири години се очаква да бъдат налични вече и 3D биопринтирани тъкани на кръвоносни съдове, специфични маломащабни възпроизвеждани тъкани на комплексни органи като бъбреци, черен дроб, панкреас. До идните седем години се планират трансплантации на биопринтирани колянни и тазобедрени стави, а до края на следващото десетилетие (Фиг. 14) стремежът е да се достигне до трансплантиране на 3D биопринтирани плътни и комплексни органи на по-достъпни цени.

Проблемът с липсата на достатъчно донори в световен мащаб (виж фиг. 15) извежда на преден план необходимоста от бързо развитие на 3D биопринтирането като една сполучлива алтернатива в това отношение. За тази цел, базирайки се на последните достижения в медицината, биотехнологиите, виртуалното прототипиране [15] и трибологията (контакнтните взаимодействия и процеси) [16], тази технология ще търпи голямо развитие и усъвършенстване и все по-широко прилагане в здравеопазването. А може би в по-далечно бъдеще ще стане факт и биопринтиране на човешко сърце (Фиг. 16).

8. ЗАКЛЮЧЕНИЕ

Статията дава в синтезиран вид обобщение на една от най-съвременните технологии базирана на достиженията на медицината и инженерните науки – 3D биопринтирането. Без претенции за детайлно представяне на информацията, тук са описани същноста, етапите на основния процес, прилаганите методи и материали за тази сравнително нова технология. Дадена е и информация за съответните инструментариум и софтуер, както и някои успешни приложения до момента в областа на тъканното инженерство, регенеративната и персонализирана медицина, проверка и разработване на лекарства и др. Специално внимание е отделено и на бъдещите очаквания в развитието на 3D биопечата предвид неговата значимост за здравеопазването на хората. Подчертана е необходимоста от интегриране на стоящите на диаметрално противоположните на пръв поглед медицина и инженерни направления като машиностроене и материалознание за подпомагане на тази авангардна технология. Очевидно научното и техническото обезпечаване на настоящето на нашия социум и особено на неговото бъдеще принадлежат на интердисциплинните научни области.

ЛИТЕРАТУРА

1. Auger F., Gibot L., Lacroix D., The Pivotal Role of Vascularization in Tissue Engineering, Annual Review of Biomedical Engineering, 2013, 15: 177–200.
2. Boland T.,"Patent US7051654: Ink-jet printing of viable cells, Google Patents.
3. Kesti M., Müller M., Becher J., Schnabelrauch M., d'Este M., Eglin D., Zenobi-Wong M., A versatile bioink for three-dimensional printing of cellular scaffolds based on thermally and phototriggered tandem gelation. Acta Biomaterialia. 2015, 11: 162–72.
4. Bajaj P., Schweller R., Khademhosseini A., West J., Bashir R., 3D Biofabrication Strategies for Tissue Engineering and Regenerative Medicine, Annual Review of Biomedical Engineering. 2014, 16: 247–76.
5. Murphy S., Atala A., (2014). 3D bioprinting of tissues and organs. Nature Biotechnology. 2014, 32 (8): 773–85.
6. Shafiee A., Atala A., Printing Technologies for Medical Applications, Trends in Molecular Medicine, 2016, **22** (3): 254–265.
7. Ozbolat I., Bioprinting scale-up tissue and organ constructs for transplantation, Trends in Biotechnology. 2015, 33 (7): 395–400.
8. Harmon K., A sweet solution for replacing organs, Scientific American. 2013, 308 (4): 54–55.
9. Yoo J., Atala A, Bioprinting: 3D printing comes to life, Manufacturing Engineering., 2015.
10. Manappallil J., Basic Dental Materials, JP Medical Ltd, 2015.
11. Станчева К., Манолева К., Биопринтинг, София, МА, УНСС, 2011.
12. 3D Printing Technology at the Service of Health (http://www.healthyeve.com/3d-printing-technology-service-health/).Graspers, 2018.

13. Bioprinting Software Suite (https://www.regenhu.com/3d-bioprinters/), RegenHu Biosystem Architects.
14. Barnatt Chr., Bioprinting, A Guide for the Future, ExplainingTheFuture.com, 2016.
15. Тодоров Г., Виртуално и физическо прототипиране, Автореферат на дисертация за получаване на научна степен „доктор на науките”, ТУ София, 2019.
16. Кандева М., Контактният подход в инженерната трибология, монография, ТУ София, 2012.

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3D BIOPRINTING FOR TISSUE ENGINEERING

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Abstract: *The paper briefly presents the essence of three-dimensional bioprinting of human tissues. Information is given about the steps of the basic process, the methods and materials used for this relatively new technology. Some successful applications of 3D bioprinting are represented and expectations for its future development are outlined. The importance of bioprinting as an impetus for new industrial convergence of medical professionals and engineers from different fields is shown.*

Keywords: *3D bioprinting, biomaterials, tissue engineering*

Tribological Journal BULTRIB Vol. 7, 2018
Papers from the 13th International Conference **BULTRIB '18**
25-27 October 2018, Sofia, Bulgaria
Society of Bulgarian Tribologists
FIT – Technical University of Sofia

EQUIVALENT VISCOUS DAMPING FOR FRICTION IN GEAR TRAIN

Stefan GARABITOV

Abstract: *An energy method was proposed to calculate the mesh damping using friction. The calculation result showed how to model vibrations of gears. The mesh damping was presented as a function. As a pattern to which the results were derived, the mathematical model of the gear tooting was used, in which the characteristics of the gearing were modeled with a non-continuous function describing friction zone. The numerical results revealed that the gear system primarily performs a non-harmonic-single-periodic motion.*
Keywords: *gear mesh; gear tooting; mesh damping; friction; nonlinear dynamics*

1. INTRODUCTION

For a better understanding of dynamic gear behavior and gear damage analysis, dynamic modeling of the vibration of the gear is widely used. The main source of vibration in a geared transmission system is usually the meshing action of the gears. The vibration models of the gear-pair in the mesh have been developed taking into account the most important dynamic factors such as the effects of the friction forces at the meshing interface, gear-backlash, the time-varying mesh stiffness, and the excitation from gear transmission errors [2]. Mostly used a dynamic model of a pair of gears is shown (see Fig. 1) [3]. The gear mesh is modeled as a pair of rigid disks connected by a spring-damper set along the line of contact.

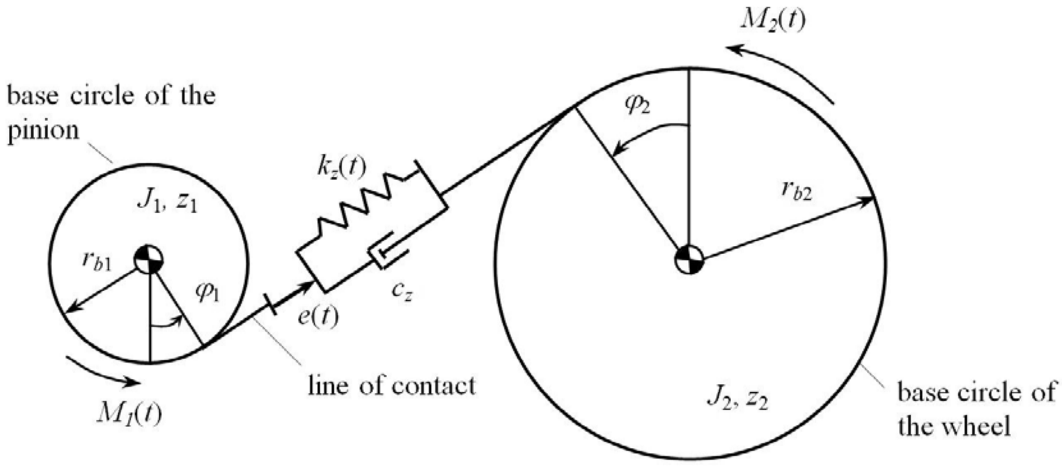

Fig. 1. Dynamic model of a pair of gears

Determination of the coefficient k_z is easy using methods of finite elements. More difficulty offers calculation damper coefficient c_z . Damping in the gear system usually is an unknown quantity, but it has an important effect in resonance vibration. In the gear train, the main energy losses are friction in the teeth meshing. damping dissipates energy constantly because of sliding friction. The magnitude of sliding friction is a constant value, independent of surface areas, displacement or position, and velocity. The system undergoing damping is periodic or oscillating and restrained by the sliding friction

2. BASICS OF THE EQUIVALENT VISCOUS DAMPING

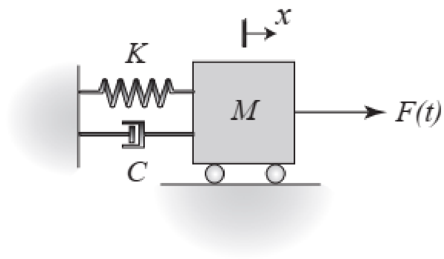

Fig. 2. Forced mass-spring-damper system (3)

The energy lost per cycle in a damper in a harmonically forced system may be expressed as:

$$W_d = \oint F_d dx, \tag{1}$$

where F_d . represents the damping force. The simplest case mathematically is that of viscous damping where $F_d = c\dot{x}$. Letting the steady-state solution be expressed as

$$x = X \sin(\omega t) \tag{2}$$

$$\dot{x} = \omega X \cos(\omega t) \tag{3}$$

$$W_d = \oint c\dot{x}\, dx = \oint c\dot{x}^2\, dt \tag{4}$$

$$W_d = C\omega^2 (kX)^2 \int_0^{2\pi/\omega} \cos^2(\omega t)\, dt = \pi C\omega (kX)^2 \tag{5}$$

3. PROBLEM

The problem is that the friction is not in the direction of movement. The friction occurs on the teeth surfaces in the area of engagement and is in the direction of the common tangent which is different from the teeth engagement. The relationship between the two displacements must be determined to determine the equivalent friction power loss in the model. Defining the ratio occurs in contact of working surfaces of the gears.

$$h = \frac{v_{slid}}{\dot{x}} = \frac{y}{x} \tag{6}$$

$$y = hX \sin(\omega t) \tag{7}$$

$$\dot{y} = h\omega X \cos(\omega t) \tag{8}$$

$$W_d = \oint C\dot{y} dx = \oint C(h\dot{x})^2\, dt \tag{9}$$

$$W_d = C\omega^2 (hX)^2 \int_0^{2\pi/\omega} \cos^2(\omega t)\, dt = \pi C\omega (hX)^2 \tag{10}$$

$$C = \frac{W_d}{\pi\omega (hX)^2} \tag{11}$$

4. EQUIVALENT VISCOUS DAMPING FOR FRICTION

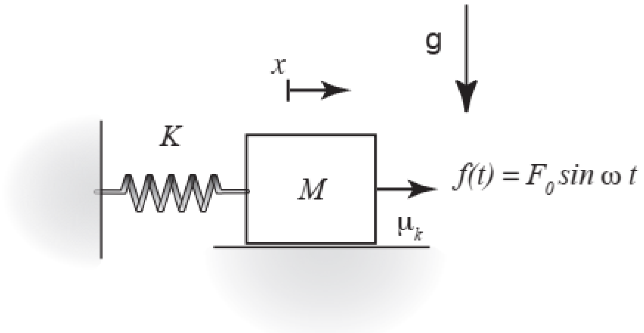

Fig. 3. Simple friction model

The resistance force, F_c, in the case of friction dissipates W_c=4FcX in energy over each quarter cycle as shown in Figure 4, hence, equating the total dissipative work per cycle to that done by a viscous damper, we have

$$W_c = 4F_c hX = \pi c\omega\left(hX\right)^2 \tag{12}$$

$$c = \frac{4F_c}{\pi\omega hX} \tag{13}$$

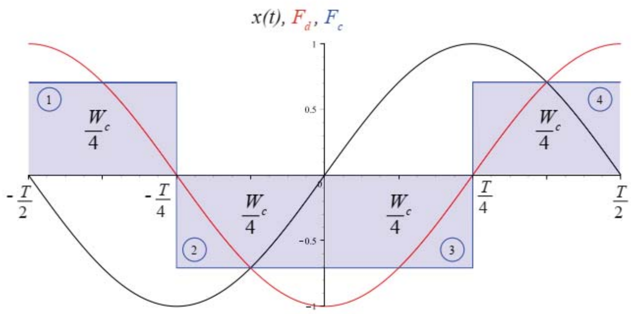

Fig. 4. Normalized viscous and friction resistance force, and displacement over one period. (3)

5. DEFINING THE RATIO

$$h = \frac{|v_{sl}|}{|\dot{x}|} = \frac{|\dot{y}|}{|\dot{x}|} = \frac{y}{x} \tag{14}$$

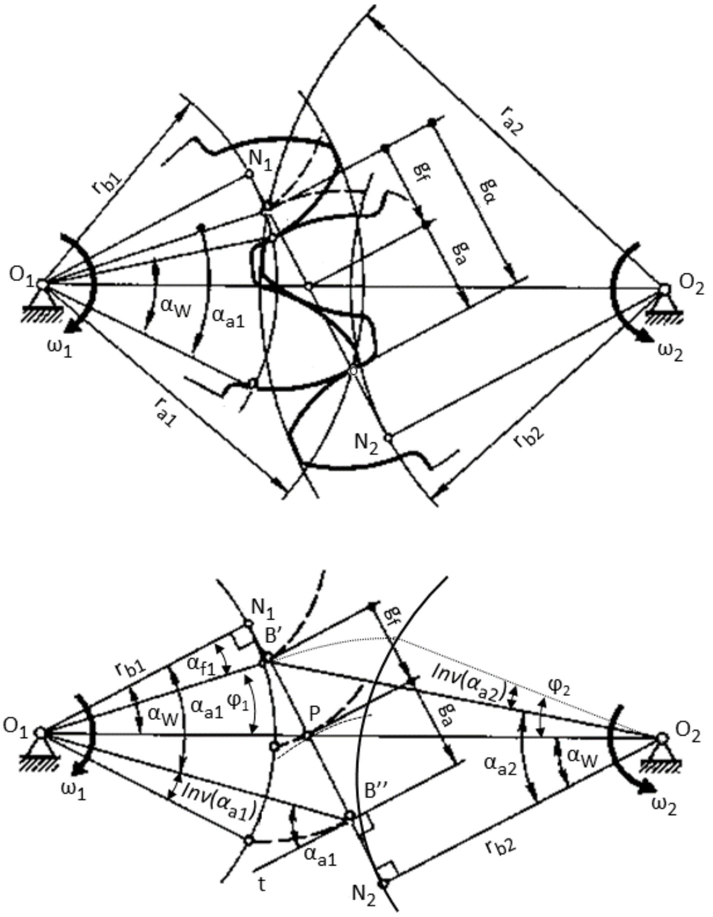

Fig. 5. Geometry of gearing

All characters in the formulas 14 to 20 for the theory of gear tooting correspond to [1]:

$$\varphi_1 = \alpha_w - \alpha_{f_1} - \nu_{\alpha_{f_1}} \tag{15}$$

$$\alpha_1 = \alpha_w - \varphi_1 - \nu_{\alpha_{f_1}} - \omega_1 t \tag{16}$$

$$\varphi_1 \in \left[\alpha_w - \alpha_{f_1} - inv\left(\alpha_{f_1}\right); -\left(\alpha_{a_1} - \alpha_w + inv\left(\alpha_{a_1}\right)\right)\right] \Rightarrow$$
$$t \in \left[0, \frac{\left(-\alpha_{a_1} - inv\left(\alpha_{a_1}\right) + \alpha_{f_1} + inv\left(\alpha_{f_1}\right)\right)}{\omega_1}\right] \tag{17}$$

$$\varphi_2 = -\alpha_w + \alpha_{a_2} + \nu_{\alpha_{a_2}} \tag{18}$$

$$\alpha_2 = \alpha_w + \varphi_2 - \nu_{\alpha_{a_2}} - \omega_2 t \tag{19}$$

$$t\left[0, \frac{\left(-\alpha_{a_1} - inv\left(\alpha_{a_1}\right) + \alpha_{f_1} + inv\left(\alpha_{f_1}\right)\right)}{\omega_1}\right] \tag{20}$$

$$\cos\left(\alpha_y\right) = \frac{r_b}{r_y} \Rightarrow \alpha_y = \text{Arccos}\left(\frac{r_b}{r_y}\right) \tag{21}$$

The radii of curvature and the slip velocity are respectively (1):

$$\rho_1 = r_{b_1} tg\left(\alpha_1\right) \quad (22)$$

$$\rho_2 = r_{b_2} tg\left(\alpha_2\right) \quad (23)$$

Relative sliding speed is:

$$\vec{v}_{sl} = \rho_1\vec{\omega}_1 - \rho_2\vec{\omega}_2 = \rho_1\vec{\omega}_1 - \rho_2 i_{21}\vec{\omega}_1 \quad (24)$$

$$k = \frac{\left|v_{sl}\right|}{\left|\dot{x}\right|} \quad (25)$$

$$\dot{x} = r_{b_1}\omega_1 \quad (26)$$

$$\vec{F}_n = \frac{\vec{T}_1}{r_{b_1}} \quad (27)$$

Friction force is:

$$F_c = \mu F_n \quad (28)$$

$$F_c = \mu\vec{F}_n\vec{v}_{sl} = \mu\vec{F}_n\left(\rho_1\vec{\omega}_1 - \rho_2 i_{21}\vec{\omega}_1\right) \quad (29)$$

The total dissipative work per cycle to that done by a damper is:

$$W_c = \oint F_c dx \quad (30)$$

Vibrating of the model mass is:

$$M\ddot{x} + c\dot{x} + Kx = F_0 \sin\left(\omega t\right) \quad (31)$$

The steady-state magnitude may be written:

$$\left|X\right| = \frac{F_0}{\sqrt{\left(K - M\omega^2\right)^2 + c^2\omega^2}} \quad (32)$$

$$\left|X\right| = \frac{\sqrt{F_o^2\pi^2h^2 - 16F_c^2}}{\pi h\sqrt{\left(K^2 - M\omega^2\right)^2}} \quad (33)$$

$$\left|X\right| = \frac{F_0\sqrt{1 - \frac{16F_c^2}{F_o^2\pi^2h^2}}}{K\left(1 - \frac{\omega^2}{\left(K/M\right)}\right)} = \frac{F_0\sqrt{1 - \left(\frac{4F_c}{F_o\pi\ h}\right)^2}}{K\left(1 - \left(\frac{\omega}{\omega_r}\right)^2\right)} \quad (34)$$

Friction resistance force:

$$F_c \le \pi h F_0 \quad (35)$$

Coefficient of friction is:

$$\mu \le \frac{\pi h F_0}{F_n} \tag{36}$$

Note that the amplitude grows unbounded as $\omega \to \omega_n$ In addition, for real (physically meaningful) solutions:

$$\frac{4F_c}{F_o \pi \ h} \le 1 \tag{37}$$

6. NUMERIC SAMPLE

Using

Table 1. Example

Number of teeth Pinion / Gear	z	17	44	
Normal module	m_n	10	10	(mm)
Center distance (working)	a_w	305	305	(mm)
Pressure angle	α	0.348	0.348	(rad)
Tip diameter	d_a	190	460	(mm)
Reference diameter	d	170	440	(mm)
Base diameter	d_b	159,74	413,46	(mm)
Root diameter	d_f	145	415	(mm)
Operating pitch diameter	d_w	170	440	(mm)
Addendum	h_a	10	10	(mm)
Dedendum	h_f	12,5	12,5	(mm)
Tip profile angle	α_a	0,572079	0,453689	(rad)
Start profile angle	α_f	0	0,086041	(rad)

$$\varphi_1 = \alpha_w - \alpha_{f_1} - \nu_{\alpha_{f_1}} = 0.3490 \tag{38}$$

$$\alpha_1 = \alpha_w - \varphi_1 - \nu_{\alpha_{f_1}} - \omega_1 t = t \tag{39}$$

$$\varphi_2 = -\alpha_w + \alpha_{a_2} + \nu_{\alpha_{a_2}} = 0.1212 \tag{40}$$

$$\alpha_2 = \alpha_w + \varphi_2 - \nu_{\alpha_{a_2}} - \omega_2 t = 0.4363 - \frac{17}{44} t \tag{41}$$

$$t_{\max} = \frac{\left(-\alpha_{a_1} - inv\left(\alpha_{a_1}\right) + \alpha_{f_1} + inv\left(\alpha_{f_1}\right)\right)}{\omega_1} = \frac{8\pi}{45} = 0.5585 \tag{42}$$

$$\rho_1 = r_{b_1} tg(\alpha_1) = \frac{159}{2} tg(t) \tag{43}$$

$$\rho_2 = r_{b_2} tg(\alpha_2) = \frac{413}{2} tg\left(0.4363 - \frac{17}{44} t\right) \tag{44}$$

$$|\vec{v}_{sl}| = |\rho_1 \vec{\omega}_1 - \rho_2 \vec{\omega}_2| = \left|\rho_1 - \rho_2 \frac{17}{44}\right| = \left|-\frac{3485}{44} tg\left(0.4363 - \frac{17}{44} t\right) + 79 tg(t)\right| \tag{45}$$

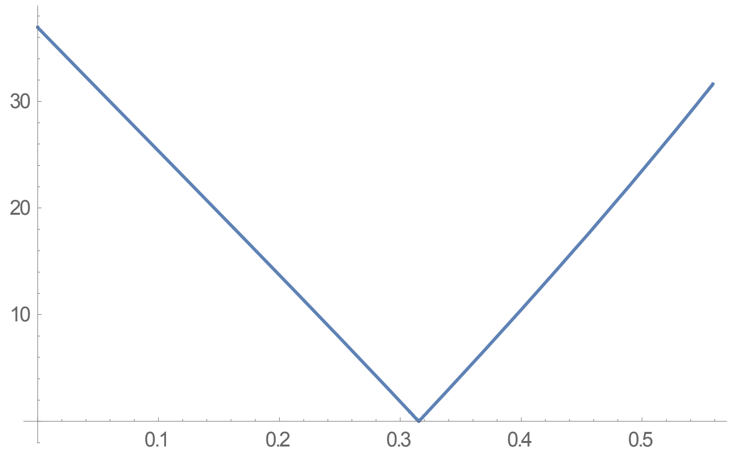

Fig. 4. Glide speed during engagement

$$\int_0^{t_{\max}} v_{sl} dt = 9.6 \tag{46}$$

$$\bar{v}_{sl} = \frac{\int_0^{t_{\max}} v_{sl} dt}{t_{\max}} = 17.1985 \, {}^{mm}\!/_{sek} \tag{47}$$

$$h = \frac{\bar{v}_{sl}}{r_{b_1} \omega_1} = 0.22 \tag{48}$$

$$T_1 = 25882 Nmm \Rightarrow F_n = 323 N \tag{49}$$

$$\mu = 0.1 \tag{50}$$

$F_c = 1.625 \mu F_n = 52.49 N$ overlap factor 1.2

The final form of the formula for determining dissipation is obtained from formulas (1) to (50) and has the following form:

$$c = \frac{4 F_c}{\pi \omega h X} \tag{51}$$

7. CONCLUSION

Formula (51) enables the calculation of dissipation with acceptable accuracy with further use to calculate the amplitudes of the natural and forced frequencies

As a pattern to which the results were derived, the mathematical model of the gear tooting was used, in which the characteristics of the gearing were modeled with a non-continuous function describing friction zone.

The analysis was carried out for the zero initial conditions (correction of teeth is zero) which allowed more easy calculations for all considered values of the system parameters.

The source of the excited mechanical vibrations of meshing gear teeth is the so-called performance and location errors. They are mainly caused by radial beating and geometric deviations of the tooth profile. This parameter depends on the accuracy of the production and assembly of the cooperating wheels. The entire mentioned factors mean that the phenomenon of energy dissipation in cooperating toothed wheels is a complex issue. However, due to the complexity of the energy dissipation phenomenon in meshing, the energy losses are usually modeled with a viscous damper. Taking into account these factors leads to a nonlinear mathematical model of a gear transmission in which chaotic phenomena may occur.

REFERENCES

1. КОНСТАНТИНОВ М., ВРИГАЗОВ А., СТАНЧЕВ Е., НЕДЕЛЧЕВ И., Теория на механизмите и машините, Техника (1980).
2. DUDLEY D. W., Gear handbook the design, manufacture, and application of gears, New York, McGraw-Hill (1962).
3. FIEBIG W., KORZYB M., Vibration and dynamic loads in external gear pumps. https://doi.org/10.1016/j.acme.2014.11.003.
4. YANGSHOU X., KANG H., FENGWEI X., YONG Y., MENG S., HUA Z., Research on the Influence of Backlash on Mesh Stiffness and the Nonlinear Dynamics of Spur Gears, Open Access Journals, https://www.mdpi.com/ .
5. NGUYEN V. K., NGUYEN P. D., Parametric Vibration Analysis of Transmission Mechanisms Using Numerical Methods, https://www.intechopen.com/.
6. ZHOU J., SUN W., YUAN L., Nonlinear vibroimpact characteristics of a planetary gear transmission system. Shock Vib. (2016). https://doi.org/10.1155/2016/4304525.
7. DANIEL DR., STUTTS S., Equivalent Viscous Damping, http://web.mst.edu/~stutts/SupplementalNotes/EqivalentViscousDamping.pdf.
8. MARGIELEWICZ J., GĄSKA D., Nonlinear Dynamics, July 2019, Volume 97, Issue 1, pp 355–368, Modelling of the gear backlash.

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Tribological Journal BULTRIB Vol. 7, 2018
Papers from the 13th International Conference **BULTRIB '18**
25-27 October 2018, Sofia, Bulgaria
Society of Bulgarian Tribologists
FIT – Technical University of Sofia

SPACE APPLICATION OF ELECTROLESS NICKEL COATING

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Grzegorz CIESLAK
Anna MAZUREK

Abstract: *Some characteristics of electroless nickel coatings plated on aluminium alloy after a stay of two years and four months outside* of the ISS *are presented in this paper. Nickel coating is produced by a technology for preliminary treatment and electroless nickel deposition developed on the base of EFTTOM-NICKEL Method. The deposition rate, determined by coatings thickness measured per an hour, is assessed on 17, 67 µm. Test for metallographic and SEM observation, EDEX analysis, also microhardness and thickness determination are performed. The results show that the coatings retain its good appearance after being in space. They are uniform, dense, without defects when the observation by means of a digital microscope is carried out. Nickel layer follows the topography of the substrate. EDEX analysis shows the presence of* phosphorous about 5, 53 mass. %, which is lower than that in the nickel coating deposited on steel or iron substrates.

The study proves the perspective for application of electroless nickel coating as a suitable material in the space industry.

KeywWords: *electroless nickel coatings, aluminium alloy, hardness, space application.*

1. INTRODUCTION

The opportunity for materials modification by surface plating gives an advantage to expand their application by gaining novel, unique properties. One of the preferred methods in this direction is electroless plating and especially electroless nickel plating. Without external power source the electroless plating ensures to obtain thickness uniformity all over the complex components and a good coating adhesion to the substrate that acquire excellent functional properties such as high wear and corrosion resistance, increase hardness, contact fatigue. The process allows maintaining a constant mode of operation and preserving the qualities of the coating over time. The technology also allows improving the reliability and consistency of the process, resulting in increased productivity of the original parts not only in the ground conditions, but also in the aviation and space industries [1].

The coatings are used on bearing journals, servo valves, compressor blades, turbine blades, pistons, engine shafts, engine mounts, landing gear, hydraulic and manifold systems, gyroscope components and optics. On jet engines, they are used on fuel control assemblies and bellows and in the space program, also they have effectively usage on the docking, cargo bay and rudder mechanisms of the space shuttle [2, 3].

Especially useful in preventing the leakage of the compressed air between the rotating and stationary parts in the high pressure compressor spacers is high phosphorus electroless nickel [4]. This is due to ensuring the uniform coating for protection of these parts. Also high phosphorus electroless nickel characteristics as a high strength, obtained by applying on a strong, light metal such as aluminum or beryllium, leads to an expanding use in space applications [2, 7].

High corrosion and wear performance and a good lubricity of the nickel coatings and the excellent performance of composite nickel coatings makes them suitable for use in the space shuttle components [5, 6].

Aluminum alloys are widely used in aerospace and allied fields due to their inherent lightness, high strength to weight ratio, excellent thermal and electrical conductance, good reflectivity and low working cost [8 - 11]. Application of aluminium alloys in these fields leads to a reduction in the structural mass resulting in a higher payload capability and higher fuel mass and from here in a longer spacecraft life. Among the conventional structural material used in space application aluminum alloys are frontrunners [12]. But the direct use of aluminum alloys is prevented by the severe influence of the operating conditions such as high specific pressure, high temperature, a corrosive environment or abrasive wear, which corrodes the aluminum surface [13, 14].

Aluminum and its alloys therefore require special surface preparation for successful use in aerospace industry for which the electroless nickel plating is an ideal opportunity [15].

The aim of this study is to investigate some characteristics of nickel coating deposited on aluminium alloy after a stay of two years and four months outside of the ISS.

2. EXPERIMENTAL PROCEDURE

The sample tested in this investigation is a part of the space experiment “Obstanovka”, carried out on the aboard of the Russian Segment of the International Space Station (RS ISS) [16].

A specially designed block called the DP-PM block made of aluminium and nickel plated is used for a container of samples for testing. Block is mounted on the outside of the ISS. After a stay of two years and four months, the DP-PM unit is dismantled and brought down to Earth in accordance with all requirements for storage and safeguarding and ensuring further safe handling of the samples. After microbiological testing and safety the box sample is subjected to examination of its properties. For the period from 04.2013 to 08.2015 the measured radiation in the space from the outside of the ISS is 425 kGy at temperature changes from - 120 ° C to + 150 ° C in 2 hours. [17].

Aluminium alloy is used as a substrate material for making the box. The composition of Aluminium alloy and microstructure are shown on Table 1 and Figure 1.

Table 1. Aluminium alloy composition

	%mass	% atom
C	4.72	10.14
O	2.68	4.31
Al	87.20	83.30
Si	0.22	0.20
Zn	5.18	2.05
Total	100.00	100.00

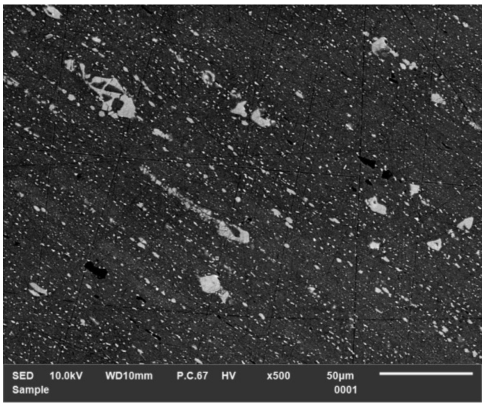

Figure 1. Microstructure of aluminium alloy

The following stages of operation are performed to obtain coatings of good quality (Figure 2):

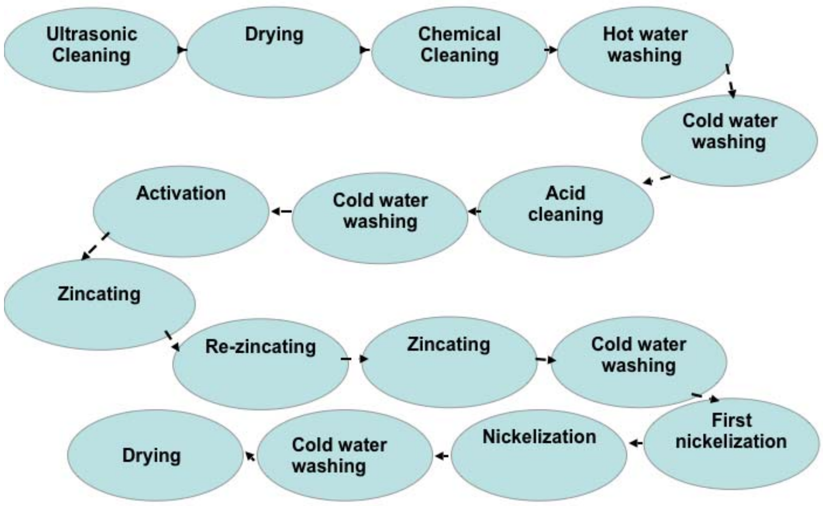

Figure 2. Stages of nickelization process

1. Ultrasonic degreasing by tri-chloroethylene at room temperature (25±5 °C) for about 20 min. depending on the grease.
2. Drying at ambient temperature
3. Chemical cleaning by alkaline solution containing sodium carbonate (Na_2CO_3), 20 g/L and trisodiumorthophosphate ($Na_3PO_4 \cdot 12H_2O$), 25 g/L operating at 60±5 °C for 2–3 min.
4. Hot water rinse
5. Cold water rinse
6. Acid cleaning for 2–3 min in a water solution of nitric acid (50:50) at room temperature (25±5 °C) for about 2-3 min.
7. Cold water rinse.
8. Activation in an old solution for nickelization
9. Zincating at ambient temperature for 15-30 min. in a solution containing ZnO, 95 - 105 g/L; sodium hydroxide, NaOH, 450 - 550 g/L
10. Zinc coating dissolving at ambient temperature for 15 - 25 sec.in HNO_3, 300 - 400 g/L
11. Zincating by repeating the step 9
12. Cold water rinse
13. Nickelization in a solution $NiCl_2.6H_2O$, 40 g/L, H_3PO_4 1 g/L at T= 40 - 50 ºC for 10 - 20 sec.

14. Electroless nickel plating in a solution EFTTOM-NICKEL now how of TU-Sofia at following conditions:

– pH = 4.6 ÷ 4.7

– T = (92 ÷ 95) ºC

– Coating time = 20 min.

– Optimal uses of the solution 7 ÷ 8 times per hour.

Chemical process of nickelization is:

$3NaH_2PO_2+3H_2O+NiSO_4 \rightarrow 3NaH_2PO_3+H_2SO_4+2H_2+Ni$

Part of the sodium hypophosphite has undergone a reduction process with phosphorous formation:

$NaH_2PO_2+H \rightarrow H_2O+NaOH+P$

Hereby the coating obtained is amorphous alloy consists of nickel and phosphorus.

The plating bath is exhausted during operation despite adherence to the technological parameters. Therefore, the solution needs to be corrected. The corrections are made every 10 minutes of the working process

15. Water rinse
16. Drying.

The samples are put to pretreatment procedure before plating including degreasing and acid pickling all the excess grease or fat and corrosion products to be removed.

After that the activation process is performed in the old Ni plating bath at the ambient temperature.

The surface activation aim is to obtain Ni nucleus on the substrate and to receive an adherent to the surface Ni-layer during the main nickelization process.

The coating microstructure is observed by means of the optic metallographic microscope Keyence VHX-5000. The samples are treated with 3 % HNO_3 – C_2H_5OH solution. The thickness of the coatings is determined. The microhardness measurements of the coatings are made by Knoop's Method using 10g load.

The coating surface observation and thickness determination are performed by SEM analysis, using Jeol JSM-IT100 LA apparatus. EDEX analysis is carried out to determine the composition of nickel coating and aluminium alloy.

3. RESULTS AND DISCUSION

The results achieved under investigation of the coatings microhardness and thickness, also coating and substrate base composition and microstructure observation are presented in Figures 3-6 and Tables 2-2.

Microhardnes measurement is performed on the part of the box sample plated for 20 minutes in the solution bath. The technological conditions are set out in our previous research [18].

Nine measurements are performed on the coating and on the substrate material and the results are averaged. The microhardness value is presented in the Table 2 and Figure 3.

The obtained results for the coatings microhardness are about eight times haigher compared to that of aluminium matrix which is consequence of the significantly stronger synergistic effect between Nickel coating and aluminium alloy on the microhardnes than this one between nickel coating and steel samples [19, 20].

Table 2. Microhardnes of Nickel coating and aluminium alloy

	HK 0,01	
	substrate	coating
	90	624
	86	572
	84	717
	80	717

	85	717
	106	683
	82	526
	84	717
	90	683
average	87	662
standard deviation	7,699206	71,60792

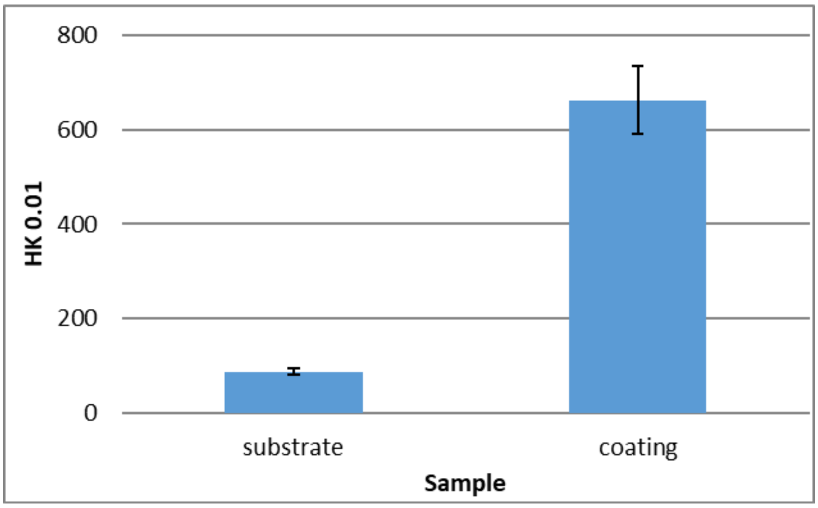

Figure 3. Microhardness of Nickel coating and aluminium alloy.

The measurement of the plating speed is performed at above mentioned technological parameters for the time of plating procedure (20 minutes) by thickness determination. Tests for the thickness measurements are carried out on 5 points (Table 3, Figure 4). The deposition rate determined for the coating thickness obtained for an hour is 17,67 µm. This speed is lower than the usually received in nickel plating on steel and cast iron [21].

Table 3. Thickness of Nickel coatings

Sample number	Thickness, µm
1	5,72
2	5,8
3	6,2
4	6,2
5	5,52
average	5,89

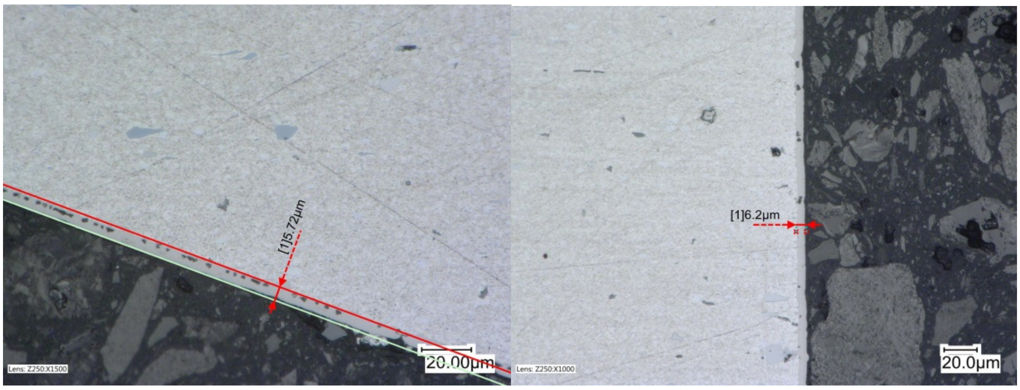

Figure 4. Metallographic observation of nickel plated aluminium alloy

The Nickel coating is found to be approximately 6μm in thickness and show good adhesion to the substrate. It is obvious the coatings can also be applied without modifying the substrate geometry and the nickel coating is the final procedure. The coatings are uniform and appears as a white strip, following the surface topography and filling defects as micro and micro cracks. The same results are observed in most of our previous works [22].

EDEX analysis, performed on the Nickel coating proves the presence not only Nickel, but phosphorous about 5, 53 mass. % (Table 4). The result is lower than that received for the coating deposited on steel and iron samples iron [23]. There is no evidence of phosphorus presence in the substrate material. Or space conditions do not promote the diffusion of phosphorus into the aluminium alloy.

Table 4. Nickel coating composition

Coatiing composition	%mass	% atom
C	2.26	9.73
P	5.53	9.21
Ni	92.21	81.06
Total	100.00	100.00

The SEM observation by EVO® MA10 „Carl Zeiss” equipped with X-Ray microanalyzer „Bruker“ shows the results confirmed the composition obtained from the EDEX analysis (Figure 5, 6).

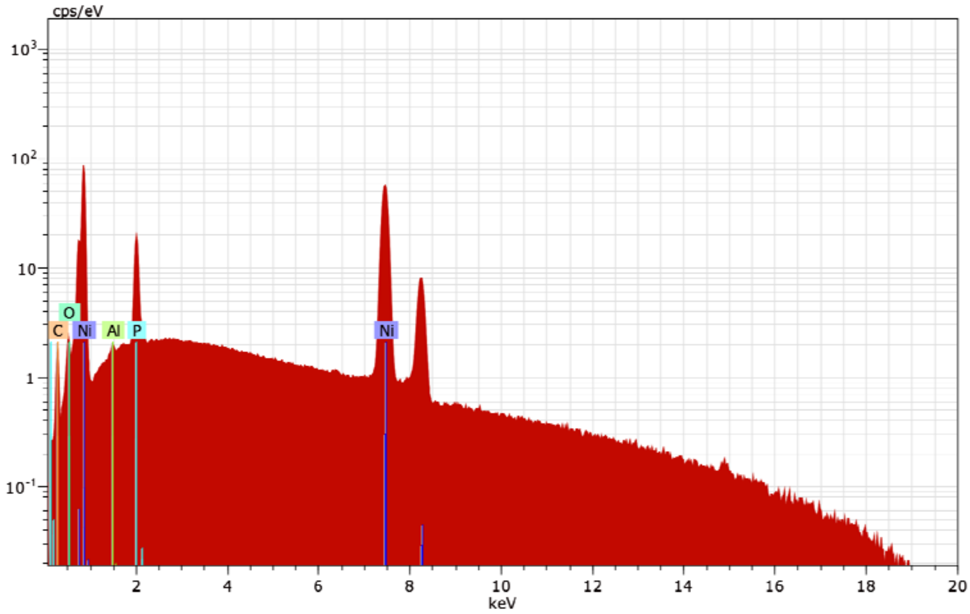

Figure 5. Chemical composition of the sample, analyzed by SEM EVO® MA10 „Carl Zeiss” equipped with X-Ray microanalyzer „Bruker“

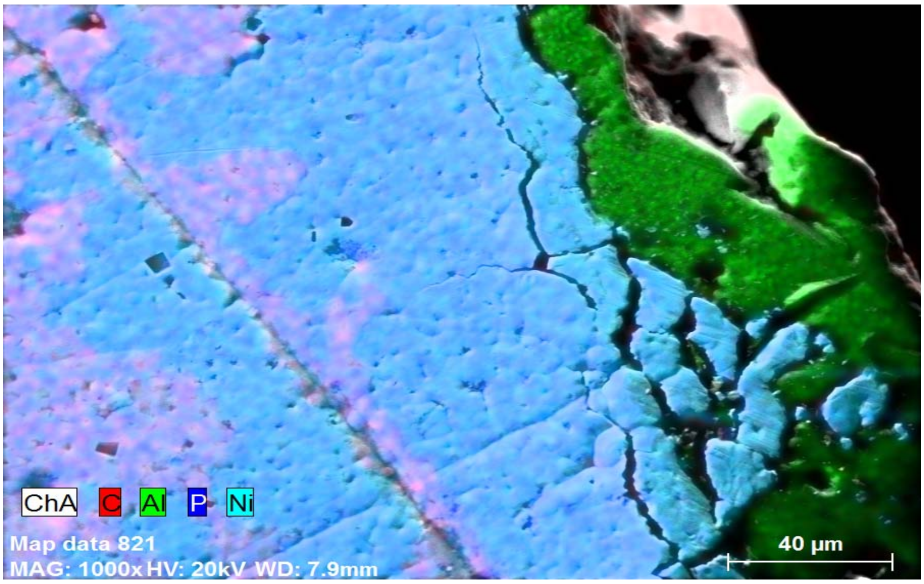

Figure 6. Microstructure observation of coated by Nickel aluminium alloy.

5. CONCLUSION

The paper is a short investigation of the surface characteristic of the sample stayed outside of the ISS two years and four months. In this period the measured radiation in the space is 425 kGy at temperature changes from - 120 ° C to + 150 ° C in 2 hours. The sample is produce from aluminium alloy coated by electroless nickel plating.

A solution for suitable pretreatment and electroless nickel plating for this alloy is developed. The obtained coating is uniform with good adhesion to the substrate material. The coatings can also be applied without modifying the substrate geometry and the nickel coating is the final procedure.

The deposition rate of nickel coating is determined to be about 17, 67 µm. This speed is lower than the usually received in nickel plating on steel and cast iron. The average coating thickness received for 20 min deposition is 5, 89 µm.

The measured microhardness value is about eight times higher compared to that of aluminium matrix which is consequence of the synergistic effect between Nickel coating and aluminium alloy.

EDEX analysis proves the presence of phosphorous about 5, 53 mass. % in Nickel matrix. The result is lower than that received for the coating deposited on steel and iron samples iron.

SEM microanalysis also proves the results received by EDEX analysis for the chemical composition of the sample.

All results obtained demonstrate that the analysed Nickel coating obtained by electroless method is promising to be used in the aerospace industry.

6. ACKNOWLEDGMENTS

This survey was partially supported by the bilateral Cooperation Agreement "Optimization of aluminium alloys surface properties with prospects for terrestrial and aero-space applications", between the Bulgarian Academy of Sciences (Space Research and Technology Institute)
and the Polish Academy of Sciences (Institute of Metallurgy and Materials Science of Polish Academy of Sciences (with support of the Institute of Precision Mechanics)).

7. REFERENCES

1. Ron Parkinson, Properties and applications of electroless nickel, Nickel Development Institute, ,https://www.nickelinstitute.org/media/1769/propertiesandapplicationsofelectrolessnickel_10081_.pdf.
2. Glenn O. Mallory, Juan B. Hajdu, Electroless Plating, AESF Society Publication, 1990.
3. Henry, M., Electroless Nickel - An Engineered Coating, Job Shop Technology, 1989.
4. Brindisi, F., The Use of Electroless Nickel in The Aerospace Industry, An Overview, S.W. Ontario Branch AESF Spring fest Symposium, Kitchener, Ontario, April 1997.
5. Henry, M., Wear-Cote International Inc., Private communication.
6. Miteva, A., Microstructure and tribology of nickel and nickel alloys, Tribological Journal BULTRIB, Vol. III, 2013, 371-375.
7.Saxena, V., Uma Rani, R., Sharma, A.K., Studies on ultrahigh solar absorber black electroless nickel coatings on aluminum alloys for space application, Surface & Coatings Technology, 201, 2006, 855–862.
8. Stark, E.A., Jr., Staley, Application of modern aluminum alloys to aircraft, J.T., Prog. Aerosp. Sci., 32, 1995, 131-172.
9.Mukhopadhyay, A.K., Sharma, A.K., Influence of Fe-bearing particles and nature of electrolyte on the hard anodizing behaviour of AA 7075 extrusion products, Surf. Coat. Technol., 92, 1997, 212-220.
10. Sharma, A.K., Rajendra, A., Gayathri, R.L., Silver Plating on Aluminium Alloys, Alum. Trans., 1 (No.1), 1999, 155-161.
11. Sharma, A.K., Gold plating on aluminium alloys for space applications, Trans. Inst. Met. Finish., 67, 1989, 87-88.
12. Sharma, A.K., Surface engineering for thermal control of spacecraft, Surf. Eng., 21 (No. 3), 2005, 249-253.
13. Celis, J.P., Drees, D., Huq, M.Z., Wu, P.Q, De bonte, M., Hybrid processes — a versatile technique to match process requirements and coating needs, Surf. Coat. Technol., 113, 1999, 165-181.
14. Wernick, S., Pinner, R., The Surface Treatment and Finishing of Aluminum and its Alloys, 4th edition, Vol. 1, Robert Draper Ltd., Teddington, UK,1972, p. 3.
15. Tulsi, S.S., Properties of electroless nickel, Trans. Inst. Met. Finish., 64, 1996, 73-76.
16. Program and methodology for acceptance tests and design and development tests of the DP instrument for measuring the potential of the ISS, NRDK, 412131.000 PM.
17. Dachev T.P., Bankov, N. G., Horneck, G., Häder, D.-P., Letter to the Editor, EXPOSE-R2 cosmic radiation time profile (Preliminary results), Radiation Protection Dosimetry, Advance Access published May 31, 2016.
18. Karaguiozova, Z., Electroless nickel composite coatings with nanodiamond additives, Journal Resource Saving Technologies for Production and Pressure Shaping of Materials in Machine-Building, Lugansk 91034, Ukraine 2014, pp. 139-145.

19. Karaguiozova Z.et all, Physical and mechanical properties of composite nickel coating, in Third Scientific Conference “SPACE, ECOLOGY, NANOTECHNOLOGY, SAFETY” with International Participation, June 2007, Varna, 324-328.
20. Kaleicheva J.K., Karaguiozova Z., Improvement of the Wear Resiatance of Ferrous Alloys by Electroless Plating of Nickel, IOP Conference Series: Materials Science and Engineering, (MSE) , 2017.
21. Karaguiozova, Z., Characterization of electroless Ni-P and electroless composite coatings Ni-P/Ni–PTFE, IJSurfSE , 12(5-6), 496–506.
22. Buchkov, D., Kaleicheva, J., Karaguiozova, Z., Antchev, V., Stavrev, S., The surface properties improvement of iron alloys be electroless composite nickel coatings, in Proceedings of the 28-th International Scientific Conference of the Faculty of Industrial Technology of TU-Sofia,“ 70 years FIT”, FIT`2015, 2015, pp.189-195.
23. Karaguiozova, Z., Characterization of electroless Ni-P and electroless composite coatings Ni-P/Ni–PTFE, IJSurfSE , 12(5-6), 2018, 496–506.

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Tribological Journal BULTRIB Vol. 7, 2018
Papers from the 13th International Conference **BULTRIB '18**
25-27 October 2018, Sofia, Bulgaria
Society of Bulgarian Tribologists
FIT – Technical University of Sofia

ELECTROLESS NICKEL COATINGS PLATED ON 2024 ALUMINIUM ALLOY

Zdravka KARAGUIOZOVA

Abstract: *The present study is based on the investigation and characterization of electroless nickel (Ni-P) coatings plated 2024 alluminium wrought alloy. The bath composition and the technological regime for electroless nickel plating are proposed applying developed EFTTOM-NICKEL method. The obtained coatings are smooth, dense and follow the topography of the substrate. The observation of coatings morphology and 3D images by means of a digital microscope HIROX KH 8700 shows thicker coatings with larger nodules formation with an increase in deposition time. It is found that thicker coatings are harder. Roughness investigation of the coatings surface indicates that growing Ni-P coating forms more irregular surface with higher peaks. The received results are encouraging for the production of aluminum alloys with improved surface characteristics*
Key Words: *electroless nickel coatings, morphology, hardness, roughness.*

1. INTRODUCTION

Thanks to the unique combination of light weight, high strength and ease of manufacture of aluminium alloys and aluminium composites they are a preferred material for application in the terrestrial and aerospace conditions.

Severe operating conditions in air and space often limit the possibility of using some of these Al alloys directly and for a long time. Therefore, in order to reduce the impact of unfavorable environmental and space conditions, for successful use in the space industry and transport, aluminum alloys and their products require special surface treatment by metal deposition.

The metal deposition on the material surfaces is well known method for improvement their properties. Improving the properties of low-cost and depleting materials is a good opportunity to expand their application areas. The possibility to produce well performing coatings, uniform over the whole substrate surface is achieved by electroless plating process. The simplicity of electroless plating technology and its ability to produce high quality coatings is the reason for their popularity in surface modification and for their application in numerous industrial fields.

The electroless plating process is conducted in an aqueous solution of a salt of the metal being deposited. The process run without external current and a selective reduction of metal ions on a catalytic substrate occurs. The formed deposit itself has a catalytic role ensuring continued deposition on the substrate, which describe the catalytic action of the plating process [1].

In the literature and industry there are sufficient data for such coatings on Al alloys, but the most extensive application finds electroless nickel coatings [2, 3].

NIckel is a preferred metal in this method for producing coatings with excellent physical and mechanical properties such as high hardness, good wear and corrosion resistance, uniform thickness all over the complicated surfaces etc. [4-10].

They are expected to replace the toxic chrome containing coatings ensuring increasing environment and working people protection [11].

The production of metallic nickel in nickel solutions by reduction with hypophosphite is discovered by Wurtz [13]. The mechanism of the chemical reaction during the process of metallization is described by Bretau,[14] Paaland Friederici,[15] Scholder and Heckel,[16] and Scholder and Haken.[17].

During extension of the work the controlled catalytic reduction of nickel ions to nickel is achieved and a high quality coatings of nickel on a steel substrate are obtained by Riddel and Brenner without the use of an external electric current [12].

The mechanism of the chemical reaction determines formation of a alloying nickel –P layer, not pure nickel [1]. The structure of Ni–P coatings depends on phosphorous quantity in the coating and on the conditions of the plating process. [18]. At low content of phosphorous in the coating (between 1–3 wt.%) a semi crystalline structure is formed and above this value the structure becomes amorphous [19-25].

[26] , [27] and [28] establish that EL Ni–P coating have a typical cauliflower-like nodular morphology, inherent for amorphous material in as-plated condition.

The difference in coating morphology is also determined depending on the composition of the boron-based or phosphorus-based reducing agent used.

Surface observation of the coatings by SEM in [29] and [30] shows the typical cauliflower-like texture [31-34] for electroless nickel-boron coatings and a faint waviness texture, apparently smoother, with bigger cells for nickel-phosphorous coatings. A lot of pores at the cell junctions in the texture of the lowP coating are defined.

[28] observes also some pores on the conventional Ni–P coating probably due to the formation of H2, whereas in work [27] the dense coatings with no porosity are obtained. The heat treatment of the coating leads to the reduction of the size of the nodules and of the volume. The nodulated surface morphology leads to the low wear and friction of EN coatings [35].

In [30] the investigation of roughness value show also dependence on the composition of nickel layer produced by reducing agent with boron or with phosphorous. The lowest Ra value is obtained for the monolayer NiB coating while Rp (mean of the 5 highest peaks) value is lower for the NiP coating, which suggests a more regular roughness. The multilayer coatings Ni-B/Ni-P have higher roughness than both the monolayers. It is obvious that the Ra value of all the coatings stays close to that of the substrate as the coating follows the topography of the substrate.

The plating bath composition influence on the phase structure and hance on the coatings hardness. [30] and [29] receive highest value for the microhardness of Nickel-boron monolayers than nickel-phosphorus. The results for multilayer coatings hardness show prevailing influence of the first layer on the hardness testing results. The hardness of the multilayer systems is closer to that of NiP than to NiB. The heat treatment of the coatings increase their hardness to varying degrees. The highest hardness value is find for LowP coating of all nickel-phosphorous coatings after heat treatment [31, 36, 37] and the worse result is obtained for high phosphorous electroless nickel.

The suggestion of the present sudy is to investigate some properties of electroless Ni-P coatings deposited on aluminium 2024 alloy to obtain material suitable to be applied both in terrestrial and in the severe space conditions.

2. EXPERIMENTAL PROCEDURE

2.1 Material and samples preparation

Substrates from aluminium 2014 alloy are produced to be undergo to plating by electroless nickel solution. The technology based on the EFTTOM-NICKEL Method is applied the nickel-phosphorous coating to be obtained as Natrium Hypophosphite is used as a reduction agent.

The samples are put to pretreatment procedure before plating including degreasing and acid pickling all the excess grease or fat and corrosion products to be removed.

After that the activation process is performed in the old Ni plating bath at the ambient temperature.

During the activation Ni nucleus are formed on the substrate surface and initiate the formation of adherent to the surface Ni-layer.

The solution for electroless plating is prepared in the composition shown in Table 1. The process conditions are also listed in Table 1.

The samples are thoroughly rinsed in de-ionized water after each of the listed processes.

Electroless nickel deposits are obtained at 4 different plating tames (10, 20, 25, 30 minutes).

2.2 Analytical methods

The morphology and 3D images observation of the coatings are performed by means of a digital microscope HIROX KH 8700.

The measurement of the coatings thickness is carried out by a digital microscope Leika BVBA and the average value of 5 measurements is determined. The data are used the kinetic of the process to be tracked.

The microhardness of the samples was assessed on polished cross sections with an automatic hardness testing machine AUTOVICK HM 200 by Knoop Method on a holding time of 20 s and a load of 0,005 g. The presented results are average value of ten measurements.

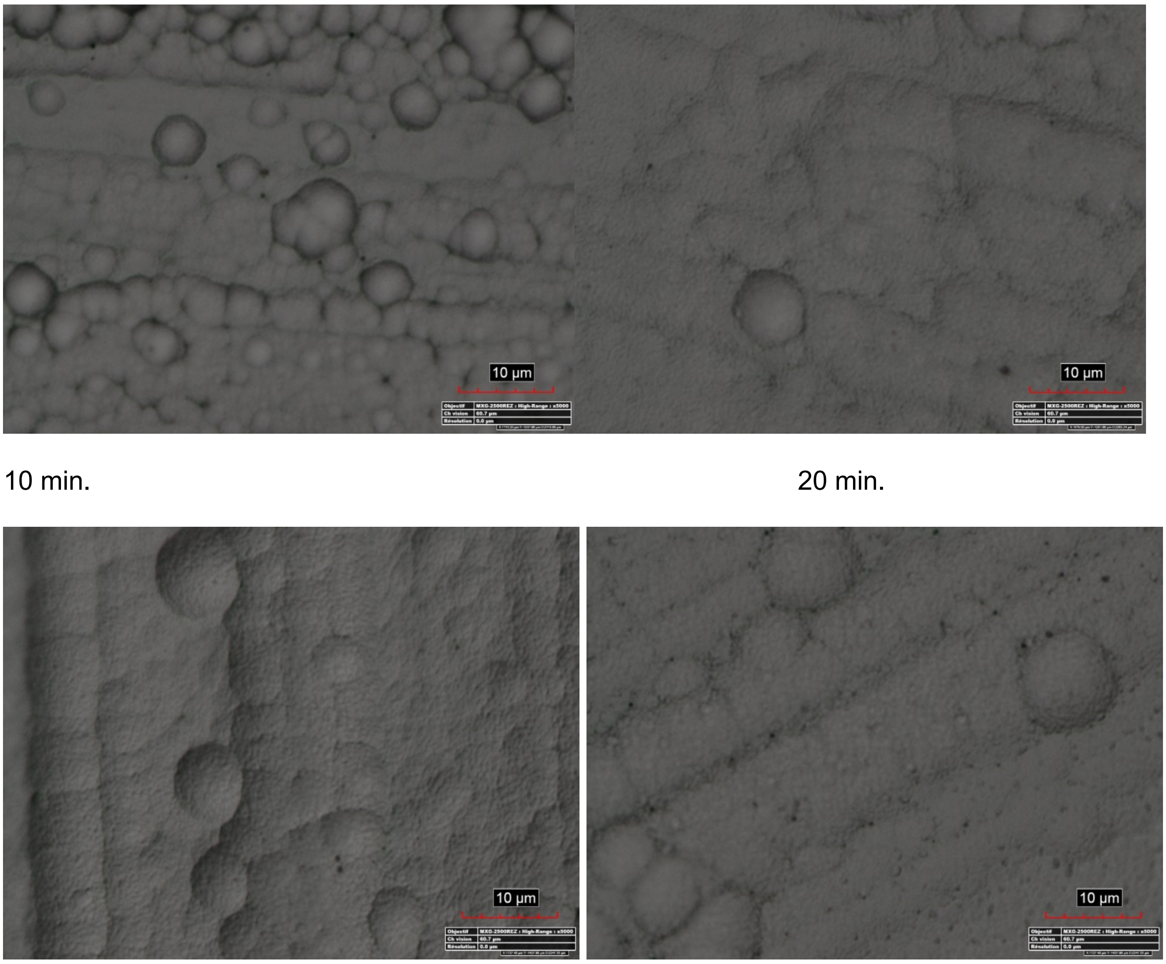
The cross sections of all of the samples are made by polishing with silicon carbide paper, then with diamond paste, to achieve a very subtle surface.

The roughness analysis is performed by a surface texture measuring instrument surfcom 14000 3DF based on the mechanical contact of a stylus with a load 0,01 N on the sample surface.

3. RESULTS AND DISCUSION

3.1. Structural and morphological characterization

Surface observation of the coatings by a digital microscope HIROX KH 8700 detects a wavelike structure with small islands above and a decreasing quantity with increasing plating time. The waves' width (corrugations) and the size of the islands show a tendency to extend with time of deposition and nodules with a cauliflower-like surface texture is observed inside them Figure 1 (a-d).



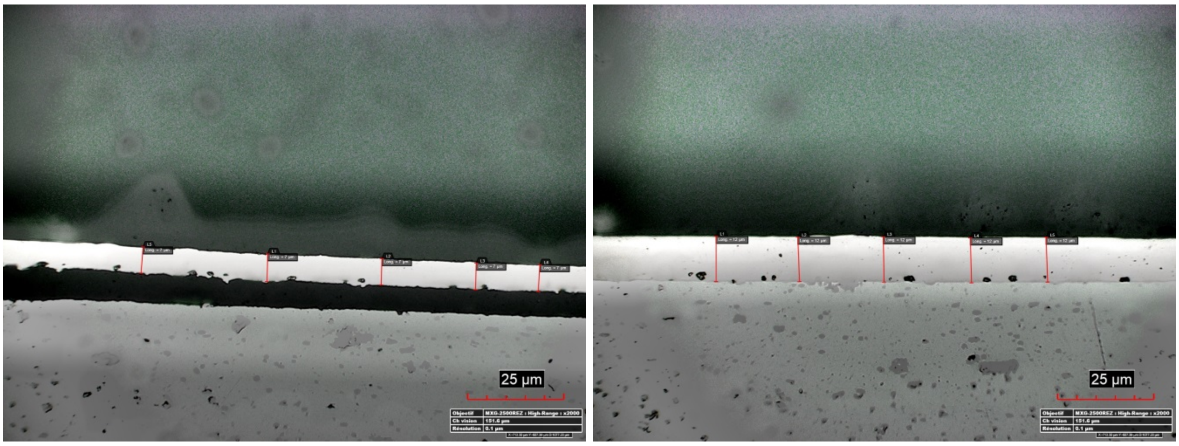
10 min. 20 min.

25 min. 30 min.

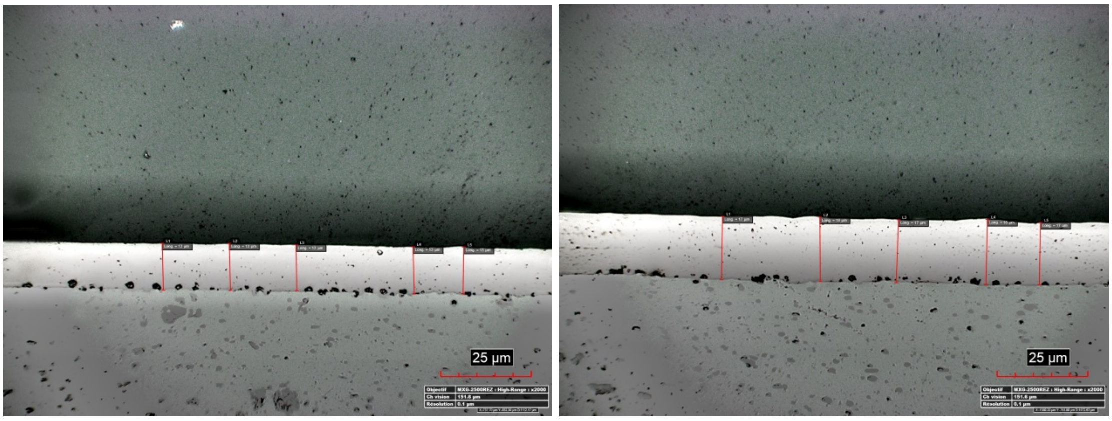
Fig. 1. Surface morphology of electroless Ni-P coating at different deposition times

Cross section of the samples presented in Figure 3 illustrates dense, uniform and smooth coatings following the surface of the substrate (Figure 3). No features inside the coatings are present.

The sample plated for 10 min shows a low adherent of the coating to the substrate. It suggested that this is due to faulty pretreatment of the sample surface.



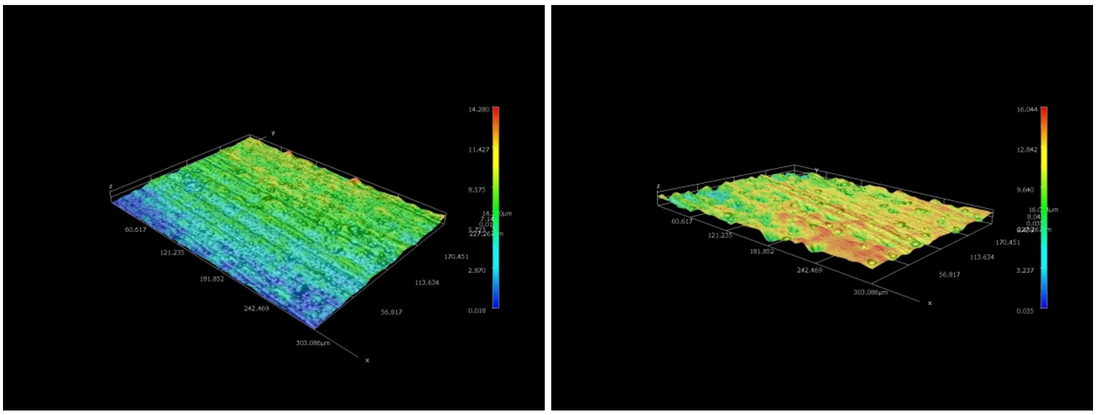
10 min. 20 min.



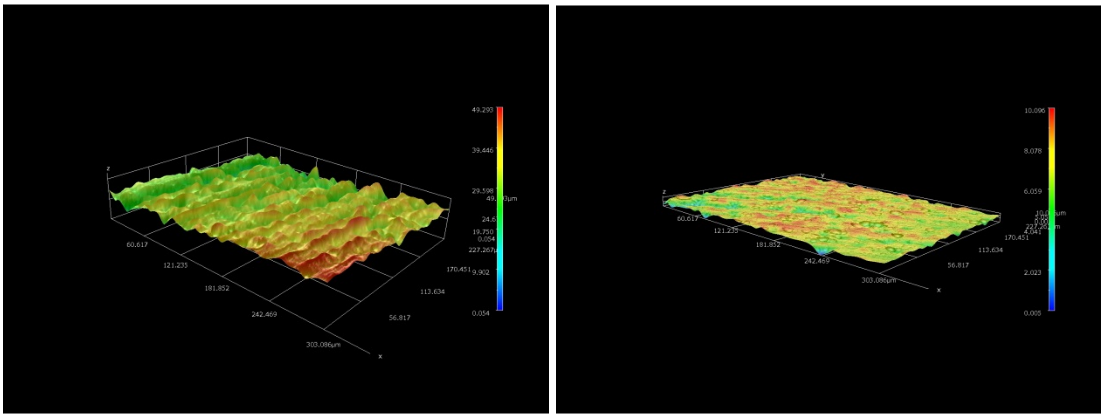
25 min. 30 min.

Fig. 4. Cross section of the samples illustrated coating view and thickness measurement

The wavelike structure and the presence of the islands above are also demonstrated on the coatings surface during observation by a digital microscope HIROX KH 8700 in Figure 2.



10 min. 20 min.



25.min. 30 min.

Fig. 2. 3D images of Ni-P coating at different deposition times at magnification x 1000

3.2. Coating thickness and hardness

The thickness of the coating defines on the cross section and no deviation is determined between 5 measurements performed (Table 1 and Figure 4). The coatings thickness increases with the plating time about 2,5 times for a half an hour. It is obvious that the average plating rate of the nickel-phosphorous deposit slowly decreases with the plating. It is slightly higher (0,7 μm/min at the beginning) than that at 30 minutes after it (0,56 μm/min). The chemicals consumption during the plating process is the supposed reason for the plating rate reduction.

Table 1. Dependence of the coating thickness on the plating time

Number of measurement	Thickness, μm			
	10min.	20min.	25min.	30min.
1	7	12	13	17
2	7	12	13	18
3	7	12	13	17
4	7	12	13	18
5	7	12	13	17
average	7	12	13	17,4

The Ni-P coatings hardness, measured by Knoop method, indicates obtaining harder coatings with increasing of the plating time (Table 2 and Figure 3). The thicker coatings have a higher hardness. But no correlation is observed between the rate of the thickness and hardness increase with the plating time. For the thickness the increase is about more than 2 times while for the hardness is only about 40%.

Table 2. Hardnes of Ni-P coatings plated in different deposition time

Number of measurement	Hardness (0,005 HK) at different plating time (min)			
1	382,4	549,7	663,3	729,0
2	492,2	651,5	710,5	663,3
3	380,7	472,6	724,3	663,3
4	433,5	460,6	571,9	706,0
5	460,6	639,4	692,8	643,3
6	420,9	511,7	655,2	729,0
7	446,7	531,7	609,6	655,2
8	422,9	465,4	710,5	655,2
9	458,2	624,3	701,6	651,2
10	431,4	440,1	701,6	697,2
average value	474,95	534,7	671,23	679,27

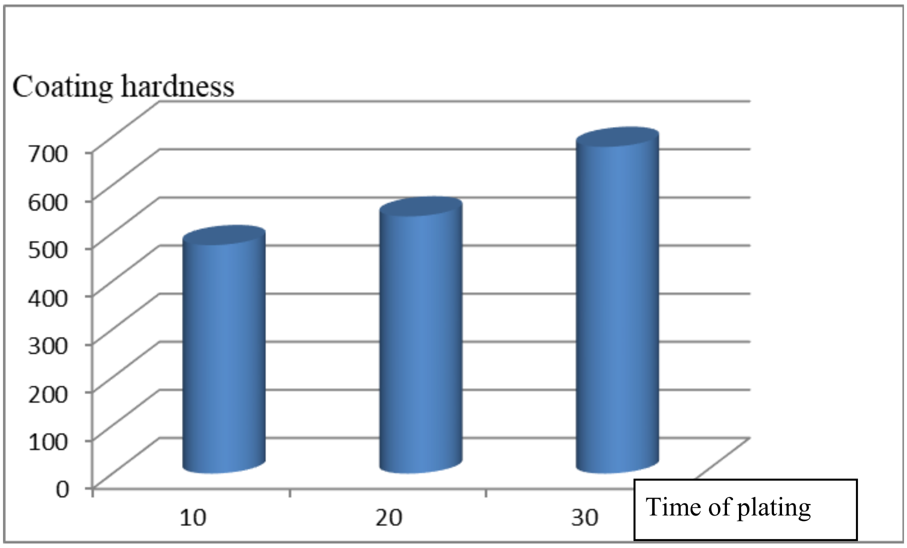


Fig. 3. Dependence of the coatings hardness on the plating time

3.3. Roughness of the coatings

The main roughness parameters arithmetical mean roughness Ra and maximum profile peak height Rp, are shoun in Table 3.

Data for Ra indicates that coatings obtained in the beginning of the plating process have lower average of the absolute values of the profile height deviations from the mean line, recorded within the evaluation length. Ra increases with the plating time. The same dependency is established for the Rp results. The growing Ni-P coating forms more irregular surface with higher peaks.

Parameter Name	Ra	Rp
sample 10 min(average value)	0,39	1,51
6	0,472143	1,97
7	0,377646	1,276667
8	0,379785	1,64
9	0,363121	1,42
10	0,355377	1,243333
sample 20 min(average value)	0,39	1,55
1	0,404127	1,506667
2	0,374991	1,166667
3	0,405032	1,293333
4	0,402238	2,46
5	0,361374	1,33
sample 25 min(average value)	0,42	1,62
11	0,399978	1,586667
12	0,44007	1,236667
13	0,396978	1,83
14	0,358698	1,163333
15	0,483275	2,306667
sample 30 min(average value)	0,56	1,63
16	0,571209	1,366667
17	0,591157	1,826667
18	0,56243	1,416667
19	0,559053	1,76
20	0,532347	1,78

Table 3. Data for the Ni-P coatings roughness at different plating time

5. CONCLUSION

Electroless nickel-phosphorous coatings deposited on samples from aluminium 2024 alloy are put under testing.

The morphology of the tested coatings corresponds to that described in the literature. Wavelike structure with small islands above is observed, changing to extension with the plating time. This view of the surface proved by 3D visualization is inherent for amorphous material in as-plated condition.

Observation of the cross sections of the coatings shows uniform, dense coatings without any futures inside. The coatings follow the substrate surface.

It is obvious that the coatings thickness increases, but the average plating rate of the nickel-phosphorous deposit slowly decreases with the plating time.

The thicker coatings have a higher hardness. But the thickness of the coating increases faster than the hardness with the deposition time.

Data for roughness parameters Ra and Rp indicate that growing Ni-P coating forms more irregular surface with higher peaks.

6. ACKNOWLEDGMENTS

Author wishes to thanks colleagues of University of Mons (metallurgy Lab) for their technical support in carrying out the tests.

The experiments are conducted under the work on the first phase of the project on the Joint Research Project on the topic “Characterization of Various Electroless Nickel Coatings (micro and nanostructured) on aluminium alloys suitable for application in terrestrial and aero-space applications”.

7. REFERENCES

1. Mallory, G.O., Hajdu, J.B., Electroless plating fundamentals and applications, American Electroplaters and surface finishers society, 1990.
2. Karaguiozova, Z., Miteva, A., Ciski, A., Cieślak, G, Some aerospace application s of aluminiumalloys, in Proceedings of the Thirteen International Scientific Conference Space, Ecology, Safety, November 2017, Sofia, pp. 327-332.
3. Colaruotolo, J. and D. Tramontana, Engineering Applications of Electroless Nickel, in: G.O. Mallory, J.B. Hajdu, Electroless Plating, American Electroplaters and surface finishers society Chapter 8, Orlando, 1990, pp. 207-227.
4. Spencer, L. F., Electroless nickel plating - a review, Metal Finishing.T2 11, 1974, pp.50-54.
5. Pearlstein F. et al., Hardness and wear resistance of eleciroless nickel-phosphorus and nlckel-boron deposits, Metal Finishing, T29, 1974, pp. 53-55
6. D.T. Gawne and U" Ma., Structure and wear of electroless nickel coatings, Materials Science and TechnoloSy, 3-3, 1987, pp. 228-238.
7. Wq Y.C.; Li, G.H.; Zhang,L., Surface Engineering 16, 2000, pp.506-510.
8. Yucheng, Wu, Zonggang, Den, I nvestigation of the Wear Resistance of Electroless Nickel-Phosphorus Alloy Plating on the Cast Iron , Materials For Mechanical Engineering,6, 1991.
9. Yamada, T., Yamamoto, A., Fujiwara M. and Kunugi, Y., Strength evaluation and effect of graphite on strength of electroless nickel plating on cast iron, Chemistry and Material Sciences 28 (1993) 3519-3522.
10. A. Miteva, “ Microstructure and tribology of nickel and nickel alloys”, Tribological Journal BULTRIB, Publ. House TU-Sofia, Sofia 2013, vol. 3, 2013, pp. 371-375.
11. Feldstein, M.D, The Environmental Benefits of Composite Electroless Nickel Coatings, Product Finishing, 8/1, 2002.
12. Brenner, A, Riddell, G. E., Nickel Plating on Steel by Chemical Reduction Part of Journal of Research of the National Bureau of Standards, Research Paper RP 1725 Vol. 37, July 1946.
13. Wurtz, M. Ad., Recherches sur la constitution des acides du phosphore, Compt. rend., 21, 149, 1845.
14. Bull. soc. chim. France (4), 9, 518 (1911).
15. Paal, C., Frederici, L., Uber die Einwirkung von Natriumhypophosphit auf wasrige Nickelsalz-Losungen, Ber. Deutschen Chem. Geselschaft, 64B, 1766, 1931.
16. Scholder R., Heckel, H., Über Schwermetallphosphide. I. Mitteilung. Einwirkung von Hypophosphit auf Nickel- und Kobaltsalze, Z. anorg. allgem. Chem. 198, 1931, pp.329-351.
17. Scholder R., Heckel, H., . Einwirkung von Hypophosphit auf Nickel- und Kobaltsalze (II Mitteil. Uber Schwermethallphosphide), Ber. Deutschen Chem. Geselschaft, 64B, 2870, 1931.
18. Szczygieł,B., Turkiewicz, A., Serafińczuk, Surface morphology and structure of Ni–P, Ni–P–ZrO2, Ni–W–P, Ni–W–P–ZrO2 coatings deposited by electroless method, Surface & Coatings Technology, 202, 2008, pp.1904–1910.
19. Martyak, N.M., Wetterer, S., Harrison, L., McNeil, M., Hen, R., Neiderer, A., Structure of electroless nickel coatings, Plating Surf. Finish., 6, 1993, pp.60-64.
20. Gao J.Q., Wu Y.T., Liu L., Shen B., Hu W.B., Crystallization temperature of amorphous electroless nickel–phosphorus alloys, Mater Lett., 59, 2005, pp.1665–1669.

21. Taheri, R., Oguocha, I.N.A., Yannacopoulos, S., Microstructure characterization of electroless NiP alloys, Can. Metall. Q. 44 (1), 2005, pp. 13-21.
22. Wang, H.C., Cai, W.B., Wang, W.I., Liu, H.T., Yu, Z.Z., Effect of Ligand on Electroless Ni - P Alloy, Surf. Coat. Technol., 168, 2003, 300-306.
23. Zhang, Y.Z., Yao, M., Studies of Electroless Nickel Deposits with Low Phosphorus Content, Trans. IMF, 77, 2, 1999, 78-83.
24. Zhang, Y.Z., Wu, Y.Y., Yao, M., Characterization of electroless Ni-P-PTFE composite deposits, J. Mater. Sci. Lett., 17, 1998, 119-122.
25. Karaguiozova, Z., Kaleicheva, J., Mishev, V., Avdeev, G., Stavrev, S., Microstructure and Properties of Electroless Composite Nickel Coatings with Nanodiamond, NANOSCIENCE & NANOTECHNOLOGY□13, eds. E. Balabanova,E. Mileva, BAS,Sofia, Bulgaria, 2014, pp. 74-77.
26. Momenzadeh, M., Sanjabi, S., The effect of TiO2 nanoparticle codeposition on microstructure and corrosion resistance of electroless Ni-P coating, Mater. Corros., Vol. 63, 7, 2012, pp. 614–619.
27. Mukhopadhyay, A., Duari, S., Barman , T.K., Sahoo , P., Wear behavior of electroless Ni-P-W coating under lubricated condition – a Taguchi based approach, IOP Conf. Series: Materials Science and Engineering 149, 2016, 012004.
28. Weiwei Chen, Wei Gao, Yedong He, A novel electroless plating of Ni–P–TiO2 nano-composite coatings, Surface & Coatings Technology, 204, 2010, pp. 2493–249.
29. Vitry, V., Sens, A., Delaunois, F., Comparison of various electroless nickel coatings on steel: structure, hardness and abrasion resistance, Materials Science Forum, Vols. 783-786, 2014, pp. 1405-1413.
30. Vitry, V., Bonin, L., Formation and characterization of multilayers borohydride and hypophosphite reduced electroless nickel deposits, Electrochimica Acta 243, 2017, pp.7–17.
31. Riedel, A., Electroless nickel plating, Finishing Publication LTD., London, 1991.
32. Riddle , Y.W., Bailer, T.O., Friction and wear reduction via an Ni-B electroless bath coating for metal alloys, JOM, 57, 4, 2005, pp. 40-45.
33. Anik, M., Körpe, E., Sen, E., Effect of coating bath composition on the properties of electroless nickel-boron films, Surf. Coat. Technol., 202, 2008, pp.1718-1727.
34. Vitry, V., Delaunois, F., Dumortier, C., Mechanical properties and scratch test resistance of nickel–boron coated aluminium alloy after heat treatments, Surf. Coat. Technol., 202, 2008, pp.3316-3324.
35. Mukhopadhyay, A., Duari, S., Barman, T. K., Sahoo, P., Application of grey fuzzy logic for the optimization of tribological performance of electroless Ni-B coating, Journal of Manufacturing Technology Research, 7, 1/2, 2015, p.1.
36. Johnson, C.E., Ogburn, F., Hardness of heat treated electroless nickel, Surf. Technol., 4, 2, 1976, pp.161-172.
37. Parkinson, R., Properties and applications of electroless nickel, Nickel Development Institute, 2001., M.: *Tribological Characterization of Advanced Dental Materials*, PhD thesis, University of Kragujevac, Faculty of Engineering, 2017.

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Tribological Journal BULTRIB Vol. 7, 2018
Papers from the 13th International Conference **BULTRIB '18**
25-27 October 2018, Sofia, Bulgaria
Society of Bulgarian Tribologists
FIT – Technical University of Sofia

EFFECTS OF DIFFERENT FINISHING PROCEDURE ONTO NANOMECHANICAL CHARACTERISTICS OF VENEERING CERAMIC

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Abstract: *This paper describes the nanomechanical characteristics of fluorapatite veneering ceramic (IPS e.max Ceram, Ivoclar Vivadent) treated with three different surface finishing procedures: polishing, glazing and grinding, using the Anton Paar nanoindentation. Also, AFM analysis of different surface finishing procedure was done in order to determine the 3D surface topography and roughness parameter Ra. The hardness (HV) and Young's modulus (E) of the surface structure were presented as results of nanoindentation measurements. Nanoindentation tests was done using Berkovich diamond pyramid and the experiment was organized in a 3x4 array. Indentation imprints were investigated using the optical and Atomic Force Microscopy. The obtained results show that the nanomechanical properties mostly depend of prepared surface finishing procedures.*

Key Words: *Nanoindentation, Fuorapatite veneering ceramic, different finishing procedure, AFM analysis.*

1. INTRODUCTION

The aesthetic and biomechanical properties of dental materials mostly depend of the distribution and particles size, as well as the concentration of the crystals in the structure of material itself [1]. Glass ceramics has become very important material in the last few years and one of the most used materials in dentistry, solely because of its excellent aesthetics, good mechanical properties and the longevity of the dental restoration itself [2].

IPS e.max Ceram is a veneering ceramic with excellent aesthetics results designed for use in conjunction with all-ceramic systems. IPS e.max Ceram is a homogeneous mixture of fluorapatite-containing glass ceramic and sintered glass powders. Veneers are thin «laminates» made of ceramic, which are attached to the tooth and which do not cover the entire tooth. Only a small amount of tooth structure is ground away for veneers. Veneering ceramics play a key role in the esthetics of a restoration. Their interplay of shade, translucency, and brightness allows for a lively appearance of the natural and restored dentition [1,3].

The mechanical properties of ceramic materials largely depend of the surface roughness and structural defects of the material itself. Porosity has a major influence on the mechanical properties of ceramic materials, where the mechanical properties of the material significantly decreasing with pronounced porosity [4]. The indentation test allows useful information's about mechanical properties of investigated material, such as hardness, Young's modulus, induced stresses, work hardening and residual thermal stresses [5,6].

The aim of this study is to identify the nanomechanical properties of veneering ceramic (*IPS e.max Ceram, Ivoclar Vivadent*), under different finishing procedure (polishing, glazing and grinding), using the Anton Paar Nanoindentation. The obtained results of nanoindentation measurements were performed in order to define the hardness (HV) and the Young's modulus (E) of the surface structure as a function of the applied indentation load. Also, AFM analysis was done in order to determine the 3D surface topography and roughness parameter Ra, for all prepared samples.

2. EXPERIMENTAL PROCEDURE

2.1. Material and samples preparation

Veneering ceramic *IPS e.max Ceram* consists of a multicomponent system SiO_2-Li_2O-Na_2O-K_2O-ZnO-Al_2O_3. The glass structure of fluorapatite is additionally strengthened by a certain wt. of the components CaO, P_2O_5 and F, (Figure 1a). These three basic components are a prerequisite for the formation of a fluorapatite crystal $Ca_5(PO_4)_3F$. Thus, the formed fluorapatite content has a big influence on the natural aesthetic appearance of restoration in the form of reflection, trasuency and opalescence. The main component of the structure is SiO_2 with ~ 60% of wt. Chemical composition of commercial Veneering ceramic *IPS e.max Ceram* is given in Table 1 [2,7].

a) b)

Fig. 1. *IPS e.max Ceram veneering ceramic.*

Table 1*. Chemical composition of Veneering ceramic IPS e.max Ceram [3].*

Standard composition	(in % by weight)
SiO_2	60 – 65
Al_2O_3	8 – 12
Na_2O	6 – 9
K_2O	6 – 8
CaO	1 – 3
ZnO	2 – 3
Li_2O	1 – 2
ZrO_2	1 – 1.5
F	1 – 2
+ Others oxides	0.5 – 7

The preparation of samples required the mold manufacturing (diameter 20 mm and height 5 mm). Before testing, all samples were firstly sintered at prescribed temperature according to manufacturer's instructions (*Ivoclar Vivadent*). After sintering, the contact surfaces of samples are prepared with 3 different finishing procedures (polishing, glazing and grinding), Figure 1b.

The 1st sample was polished on the polishing machine, under controlled speed, using diamond sandpaper with different grits (280, 400, 600, 800, 1200 and 2000) with hand pressure and water cooling. The fine polishing was done after that by using the liquid emulsion with grain size of 6 and 0.04 µm. Final roughness prior to testing was Ra=12.239 nm. The contact surface of the 2nd sample was glazed according to the manufacturer's recommendations (*Ivoclar Vivadent*). Testing roughness was Ra=17.253 nm. On the end, contact surface of the 3rd samples was grinded by using diamond borer (Medin, ISO: 806 314 146 534 016, 150 µm – max). Measured roughness of grinding sample was Ra=0.786 µm.

On the end, all samples surfaces were cleaned with 70 % alcohol before every test, in order to remove any remaining surface contaminants.

2.2. AFM analysis

All results of roughness parameter (Ra) and 3D surface topography were obtained by NT-MDT AFM microscope (Fig. 1). The measurement range on all samples is 100x100 µm. AFM have been described thoroughly in a previous publication [8].

2.2 Nanoindetation

Nanoindentation tests were done using Anton Paar Nanoindenter, which is located at the Tribology center on the Faculty of Engineering in Kragujevac (Figure 2).

Fig. 2. *Anton Paar Nanoindenter [1].*

Indentation data were obtained using loads of 50, 100, 200 and 400 mN for each samples. Maximum load holding time was 10 s. A Berkovich diamond indenter was used for all indentations. Each test was repeated three times. The study obtained values of hardness and Young's modulus.

Indentation imprints were investigated using the Optical and AFM microscopy.

3. RESULTS AND DISCUSION

Nanomechanical tests were preceded by the AFM analysis in order to determine the roughness parameters Ra and 3D topography of the tested material under different surface finishing procedure (Figure 3). Presented results, show that lowest values of R_a have polished finishing procedure, as expected.

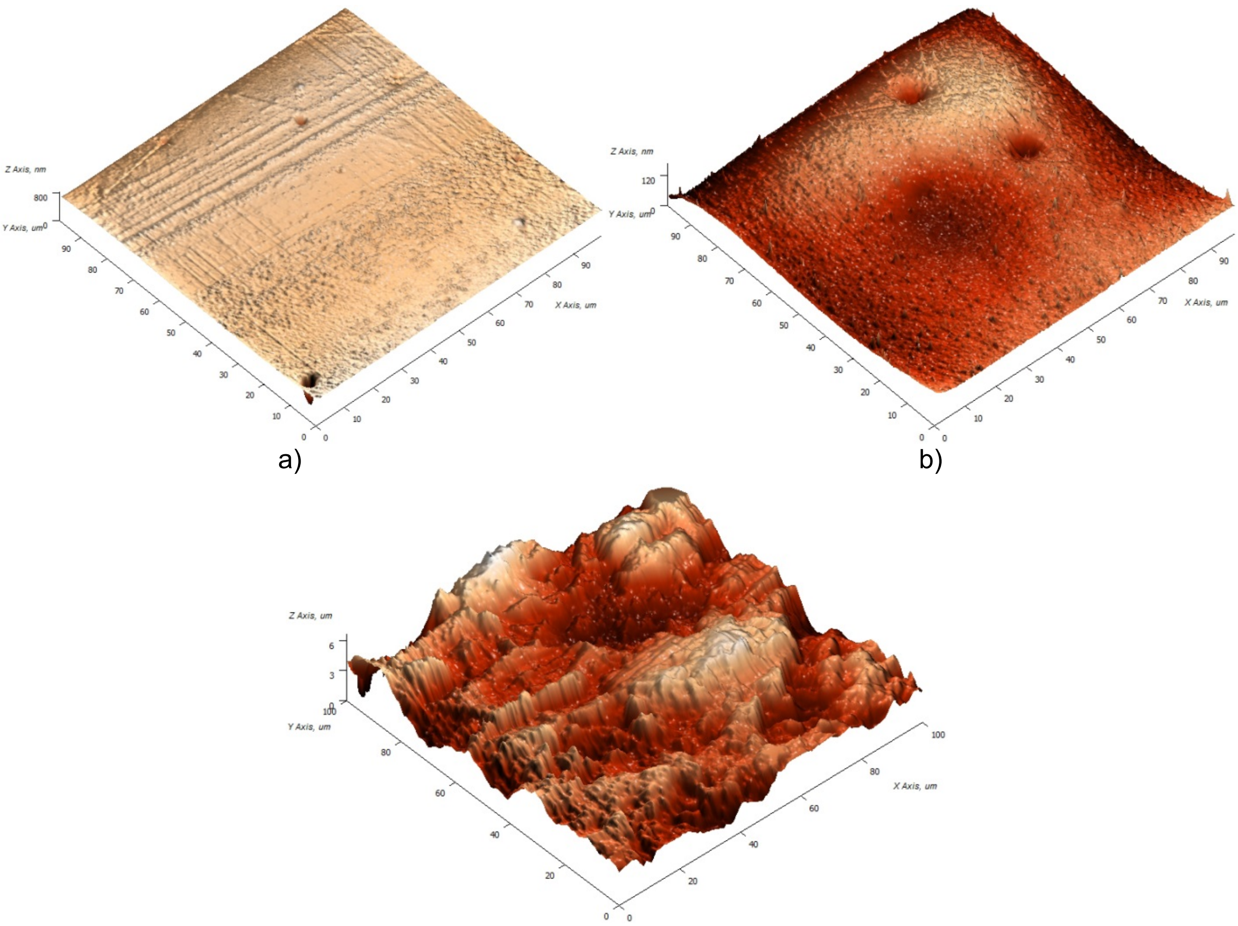


Fig. 3. *AFM analysis (3D topography) of samples: a) polished, b) glazed, and c) grinded surface.*

Surface roughness has a big influence on the many things as well as aesthetic of the contact surface of material itself, changing color on the dental restoration, secondary caries and gingival irritation, and the mutual wear of contact surfaces of teeth and antagonists (natural tooth or dental restoration). The most main goal in esthetic dentistry is that the finishing procedure of the contact surface of material should be as smooth as possible [1,2,8].

The obtained results of nanoidentation (hardness and Young's modulus) are presented at the Fig. 4. Results are presented as mean values of all measured parameters obtained as the arithmetic mean of the 3 repeated tests.

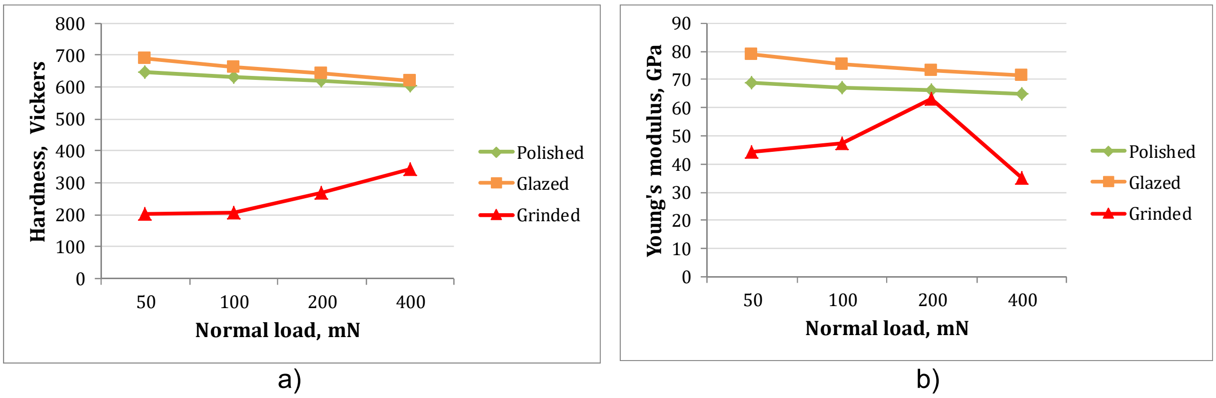


Fig. 4. *Nanoindentation results: a) Hardness (HV) and (b) Young's modulus (E).*

From the presented Figure 4 it can be clearly seen that the highest value of hardness and Young's modulus has a glazed sample. Also, is visible trend for polished and glazed surfaces that hardness and elastic modulus decreases in a very small range with increasing normal load. Grinding does not have a trend as polished and glazed surfacesses probably due to the pronounced surface roughness at the place of testing. The contact between the Berkovich indenter and the surface of the sample is realized mostly per tops of roughness. The phenomenon of decreasing hardness by increasing the indentation load is known under the term "Indentation size effect (ISE)" [10,11]. Figures 4a and 4b clearly show that the glaze has a significant impact on the obtained results, ie, provides better mechanical properties of the material itself.

Figure 5 shows the load-displacement curves for different prepared samples as mean values of three indentations for loads 50, 100, 200 and 400 mN. The curves have proper form and clearly show that it is maximum load holding time properly selected [12,13].

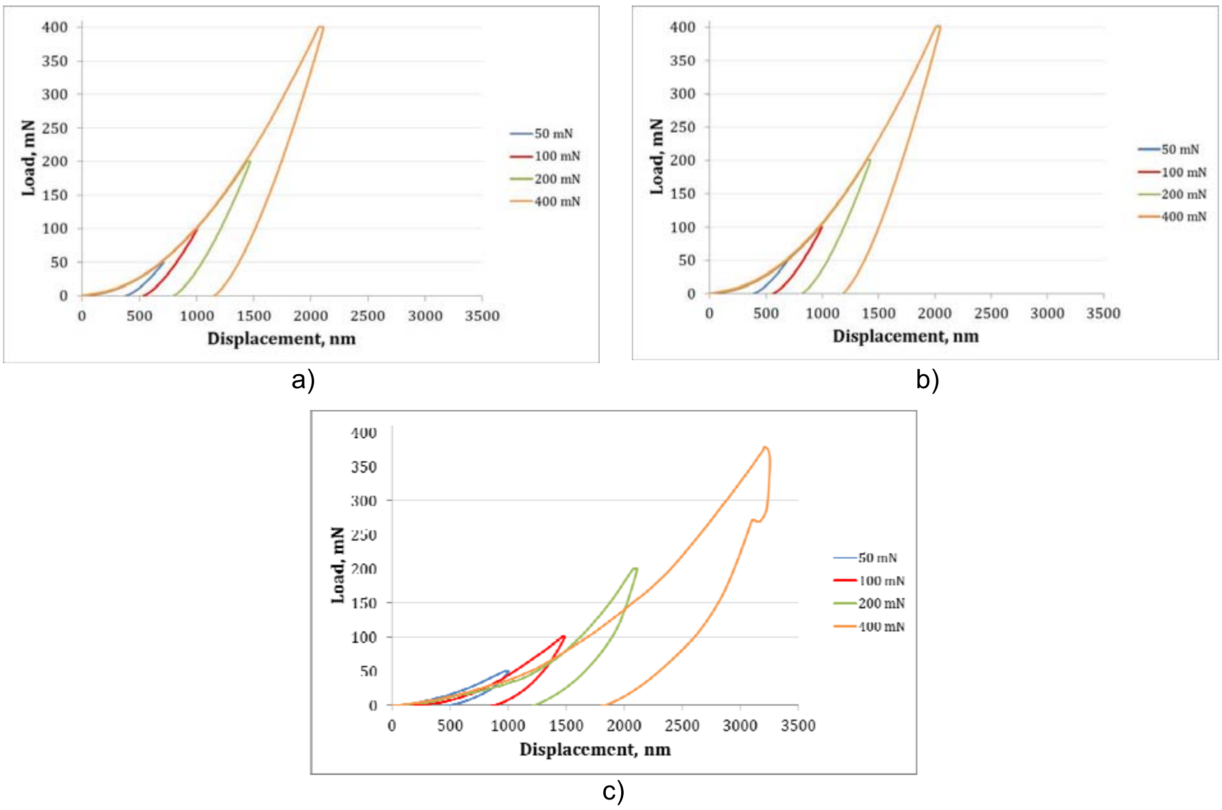
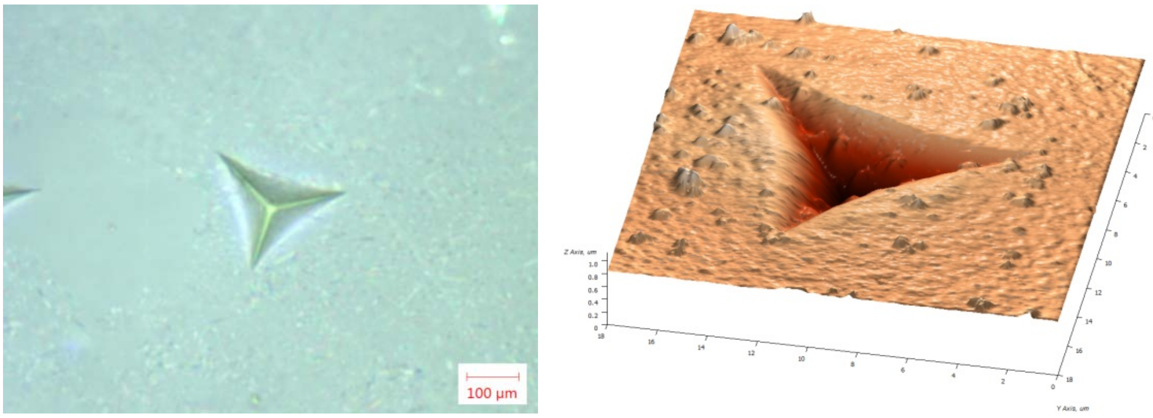


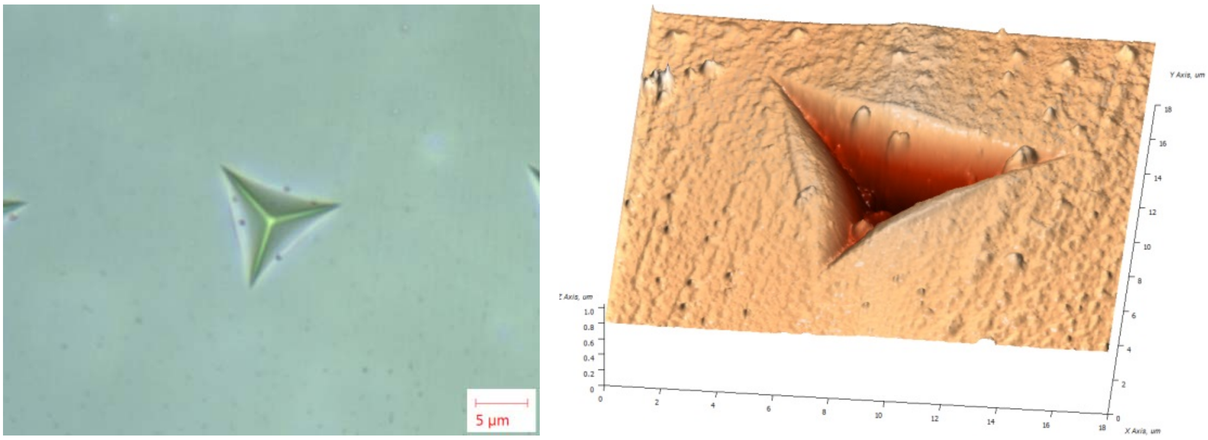
Fig. 5. *Load-displacement curves under different finishing procedure: a) polished, b) glazed and c) grinded.*

The diagrams (Figure 5) clearly show that the indentation depth proportionally increasing with the increase of normal load. There are no major differences in indentation curves for polished and glazed tested samples, while the grinding curve has a mild deviation from the previous two samples, especially in the case of a 400 mN indentation load, where is a irregular shape of the load-displacement curve result of different surface roughness in the contact zone and gas bubble occurrence in contact suraface of samples, whose presence is characteristic for this material [1].

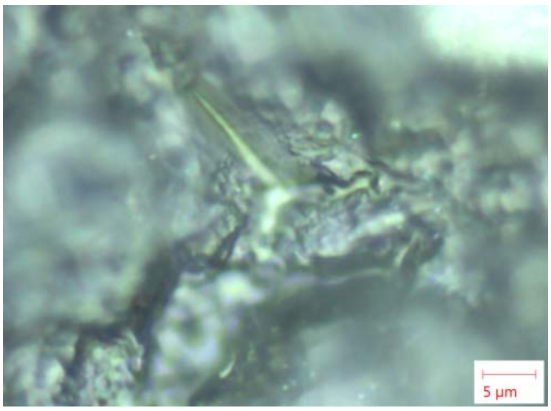
The Figure 6 shows representative indentation imprints (400 mN) of Veneering ceramic under different finishing procedure, obtained on optical (x100) and Atomic force microscopy. Nanoindentation on grinding sample was presented just by optical microscopy because it was impossible to find indentation imprints on AFM due to their small size of imprints and big surface roughness of the material.



a)



b)



c)

Fig. 6. *Indentation imprints at load of 400 mN, analysed by optical (left, x100) and AFM microscopy (right): a) polished; b) glazed and c) grinded surface.*

Indentation imprints are clearly formed with visible edges in the surface layer of material. On Figures 6a and 6b around imprints it can be noticed mild plastic deformation (brighter zone), as a result of displacement of material (piling-ups) during the penetration of indenter.

Plastic creep of material on the along the side of the indentation marks can be considered as the basic physical process softening the material due to the phenomenon of shear [14]. The reason for this is that the plastic creep of material by shearing causes certain structural changes in the field of the material itself, which means that the deformation in that zone is much faster than in the other zone of the material [15]. Materials that move from the piling-up condition to the sinking-in condition, become much more elastic [16]. This also shows the importance of the Young's modulus, which present a measure of the stiffness of the material. Since the polished and glazed surfaces are most common in practice, mechanical properties of materials has big importance on lifetime of dental restoration because they mostly depends on quality of the finishing procedure.

Presented results are in accordance with the obtained results of several similar studies [15,17-21], also they may assist in better understanding of the mechanical behaviour of Veneering ceramic under different finishing procedure and thus facilitate the design and CAD/CAM manufacture for dental restorations.

5. CONCLUSION

The mechanical properties of ceramic materials largely depend of the surface roughness and structural defects of the material itself. Based on the obtained results, it can be concluded that nanomechanical properties mostly dependent of applied surface finishing procedures.

The highest value of hardness and Young's modulus has a glazed sample. The glaze, as a finished procedure, has a significant impact on the obtained results, ie, provides better mechanical properties of the material itself.

Presented results may assist in better understanding of the nanomechanical behaviour of veneering ceramic under different finishing procedure and thus facilitate the design, selection and CAD/CAM manufacture for dental restorations.

ACKNOWLEDGMENTS

Research presented in this paper was supported by the Ministry of Education, Science and Technology Development of Republic of Serbia, Grant TR-35021.

REFERENCES

1. Pantić, M.: *Tribological Characterization of Advanced Dental Materials*, PhD thesis, University of Kragujevac, Faculty of Engineering, 2017.
2. Shen, J.Z., Kosmač, T.: *Advanced Ceramics for Dentistry*, Elsevier, USA, 2014.
3. Bühler-Zemp P., Völkel T., Scientific Documentation IPS e.max Ceram, Ivoclar-Vivadent AG, Schaan, 2005.
4. de Jager, N., Feilzer, A.J., Davidson, C.L., *The influence of surface roughness on porcelain strength*, Dent. Mater., Vol. 16, p.p. 381-388, 2000.
5. Bucaille, J., Stauss, S., Felder, E., Michler, J.: *Determination of plastic properties of metals by instrumented indentation using different sharp indenters*, Acta Materialia, Vol. 51, No. 6, p.p. 1663-1678, 2003.
6. Gouldstone, A., Chollacoop, N., Dao, M., Li, J., Minor, A., Shen, Y.: *Indentation across size scales and disciplines: Recent developments in experimentation and modeling*, Acta Materialia, Vol. 55, No. 12, p.p. 4015-4039, 2007.
7. Völkel T., Report No 17 - Research and Development Ivoclar Vivadent AG, FL-9494 Schaan / Liechtenstein, 2006.
8. Pantić, M., Mitrović, S., Babić, M., Jevremović, D., Kanjevac, T., Džunić, D., Adamović, D.: *AFM Surface Roughness and Topography Analysis of Lithium Disilicate Glass Ceramic*, Tribology in Industry, Vol. 37, No. 4, p.p. 391-399, 2015.
9. Castiglia Gonzaga, C., Francisco Cesara, P., Gomes Miranda Jr., W., Naoyuki Yoshimura, H.: *Slow crack growth and reliability of dental ceramics*, Dental Materials, Vol. 27, No. 4, p.p. 394-406, 2011.
10. Bull, S.J., Page, T.F., Yoffe, E.H.: *An explanation of the indentation size effect in ceramics*, Journal Philosophical Magazine Letters, Vol. 59, p.p. 281-288, 1989.
11. Pöhl, F., Huth, S., Theisen W.: *Detection of the indentation-size-effect (ISE) and surface hardening by analysis of the loading curvature C*, International Journal of Solids and Structures, Vol. 84, p.p. 160-166, 2016.
12. Oliver, W.C., Pharr, G.M.: *An improved technique for determining hardness and elastic modul ususing load and displacement sensing indentation experiments*, J. Mater. Res. Vol. 7, p.p. 1564–

1583, 1992.
13. Džunić, D., Mitrović, S., Babić, M., Bobić, I., Pantić, M., Adamović, D., Nedeljković. B.: *Nanoindentation of Za-27 Alloy Based Nanocomposites Reinforced with Al_2O_3 Particles*, Tribology in Industry, Vol. 37, No. 4, p.p. 413-420, 2015.
14. Sergueeva, A.V., Mara, N.A., Kuntz, J.D., Lavernia, E.J., Mukherjee, A.K.: *Shear band formation and ductility inbulk metallic glass*, Philos. Mag., Vol. 85, p.p. 2671–2687, 2005.
15. Alao, A.-R., Yin, L.: *Nano-mechanical behaviour of lithium metasilicate glass–ceramic*, Journal of the mechanical behavior of biomedical materials, Vol. 49, p.p. 162–174, 2015.
16. Alcala, J., Barone, A.C., Anglada, M.: *The influence of plastic hardening on surface deformation modes around Vickers and spherical indents*, Acta Mater., Vol. 48, p.p. 3451–3464, 2000.
17. Alao, A.-R., Yin, L.: *Loading rate effect on the mechanical behavior of zirconia in nanoindentation*, Materials Science & Engineering A, Vol. 619, p.p. 247–255, 2014.
18. Alao, A.-R., Yin, L.: *Nano-scale mechanical properties and behaviour of pre-sintered zirconia*, Journal of the mechanical behaviour of biomedical materials, Vol. 36, p.p. 21–31, 2014.
19. Smith, C.M., Jiang, D., Gong, J., Yin, L.: *Determination of the mechanical behavior of lithium disilicate glass ceramics by nanoindentation & scanning probe microscopy*, Materials Chemistry and Physics, Vol. 148, p.p. 1036-1044, 2014.
20. Arsecularatne, J.A., Dingeldein, J.P., Hoffman, M.: *An in vitro study of the wear mechanism of a leucite glass dental ceramic*, Biosurf. Biotribol., Vol. 1, p.p. 50–61, 2015.
21. Pantić, M., Mitrović, S., Babić, M., Jevremović, D., Džunić, D., Kanjevac, T., Adamović, D.: *Effects of Different Finishing Procedure onto Nanomechanical and Nanotribological Characteristics of Lithium Disilicate Glass Ceramics*, Tribological Journal BULTRIB, Vol. 6, p.p. 137-146, 2016.

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Tribological Journal BULTRIB Vol. 6, 2016
Papers from the International Conference **BULTRIB '16**
27-29 October 2016, Sofia, Bulgaria
Society of Bulgarian Tribologists
FIT – Technical University of Sofia

TRIBOLOGICAL BEHAVIOR OF ZA-27 ALLOY BASED NANOCOMPOSITE REINFORCED WITH SiC NANOPARTICLES

Dragan DžUNIĆ, Slobodan MITROVIĆ, Miroslav BABIĆ, Marko PANTIĆ, Ilija BOBIĆ

Abstract: *Dry sliding friction and wear behaviour of ZA-27 alloy nanocomposite reinforced with SiC nano particles of size 50 nm was evaluated. The content of SiC particles in the alloy was 1, 3 and 5vol. %. The nanocomposites were produced by the compocasting procedure. The SiC nanoparticles as reinforcement were added into the semi-solid ZA-27 alloy under intensive mixing. Mechanical characteristics of obtained nanocomposites were evaluated through hardness tests. A block-on-disc tribometer was used to evaluate the wear volume and friction coefficient, while 30CrNiMo8 steel disc was used as the counterface, under dry sliding conditions at different specific loads and sliding speeds. Wear tracks were examined using optical microscopy. Results indicated that hardness and wear resistance decreases with increasing the content of reinforcement in ZA-27 alloy.*
Keywords: *Wear, Friction, ZA-27, Nanocomposite*

1. INTRODUCTION

Zinc-Aluminium (ZA) alloys are widely used in numerous tribological applications and due to that this family of alloys is very attractive for researchers. Neither one other alloy does not provide such combination of strength, toughness and stiffness as casted zinc-aluminium alloys. In the beginning, content of aluminium was varied, starting from 8% [1, 2], than 12% [3] and finally 27% was proved to be the best balance of zinc and aluminium for tribological applications. Zinc-Aluminium alloys were developed to replace heavy conventional bearing bronze [2-7] and expensive aluminium alloys. These alloys contain a very small amount of copper which is the main reason why these alloys can be very economic and efficient replace for a large number of non-ferrous metals, while they possess higher strength, better wear resistance and lower casting temperature [8]. Main restriction for these alloys is working temperature. On elevated temperatures over 100°C mechanical properties of ZA alloys deteriorates [8, 9].

ZA-27 alloy is the most attractive for many researchers because of their great strength. Great mechanical and tribological properties makes them very applicable for journal bearings, thin walled castings, electrical components, automotive, industrial and agriculture machines and devices, valves etc. [10]. There are a numerous research investigation in order to improve mechanical and tribological properties of ZA-27 alloy, primary trough obtaining composite materials based on ZA-27 alloy. In order to improve frictional properties graphite as hard lubricant was added [11-13], while hard particles were added in order to improve wear resistance [14-19]. In order to combine benefits from hard particles and graphite as a hard lubricant, hybrid composite materials were developed [20]. ZA-27 alloy and their hard particle reinforced composites shown a good corrosion resistance [21-23].

This paper presents tribological investigation of nanocomposites based on ZA-27 alloy obtained by compocasting procedure. Composites are reinforced with SiC nanoparticles. Average nanoparticles size was 50 nm, while the content in the base alloy was 1, 3 and 5 vol. %. Among the various nanocomposites production procedures stirring casting is generally accepted as most cost-effective procedure and also due to mass production applicability compocasting was selected as nanocomposites obtaining procedure.

2. EXPERIMENT

2.1. Materials and method of fabrication

ZA-27 based nanocomposites reinforced with SiC nanoparticles with average size 50 nm were obtained using compocasting procedure. Chemical composition of the base ZA-27 alloy is presented in table 1. Compocasting procedure is carried out in two phases. The first phase is the preparation of semi-solid melt, then infiltration of reinforcement SiC nanoparticles (average size 50 nm) during intensive mixing of the melt. After infiltration of reinforcement nanoparticles the resulting mixture was stirred for 15 min at 1000 r/min and then it is poured in preheated mold. After cooling obtained nanocomposites are cut and then hot pressed on temperature 250°C and pressure of 350 MPa. After hot pressing, nanocomposites are cut into blocks for tribological test.

Table 1. Chemical composition of ZA-27 alloy

Alloy	Chemical composition (weight %)			
	Al	Cu	Mg	Zn
ZA-27	25-27	2 do 2,5	0,015-0,02	Balance

Before tribological tests hardness test and density measurement using Archimedes' principle were done, on base alloy and obtained nanocomposites. Hardness test was realised using diamond Vickers pyramid with normal load of 50 N. Obtained results are presented in table 2.

Table 2. Hardness and density values for tested materials

	Material	Hardness, HV_5	Density, g/cm3
1	ZA-27	122	4.845
2	ZA-27 + 1 vol% SiC	113	4.664
3	ZA-27 + 3 vol% SiC	112	4.650
4	ZA-27 + 5 vol% SiC	95,5	4.323

2.2. Tribological tests

Tribological tests were carried out in a computer aided block-on-disk sliding testing machine (developed at the Faculty of Engineering ex. Faculty of Mechanical Engineering) with the contact pair geometry in accordance with ASTM G 77–05. A schematic configuration of the test machine is shown in figure 1. More detailed description of the tribometer is available elsewhere [24].

The test blocks (6.35x15.75x10.16 mm) were prepared from obtained nanocomposite materials. The counter face (disc of 35 mm diameter and 6.35 mm thickness) was made of EN: 30CrNiMo8 steel of 62HRC hardness. The surface roughness of the counter face steel disk was Ra=0.192 μm, while the surface roughness of nanocomposites was around 0.09 μm.

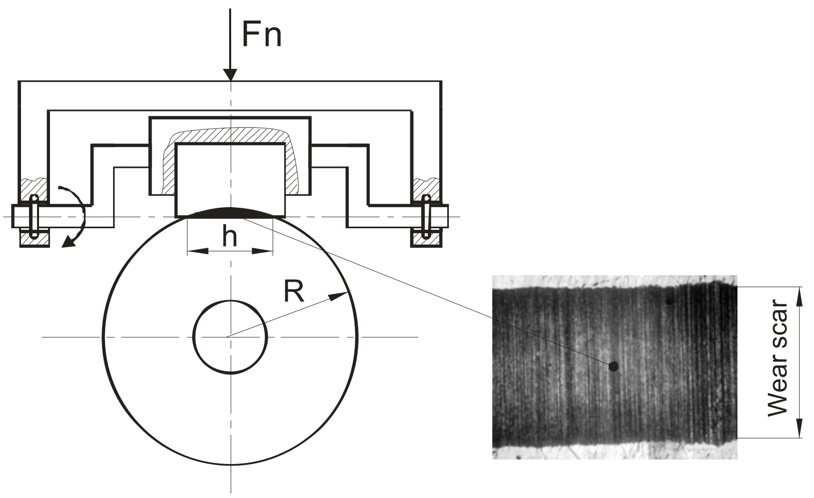


Figure 1. The scheme of contact pair geometry [24].

The tests were performed under dry sliding conditions at different sliding speeds (0.25 m/s, 0.5 m/s, 1 m/s) and applied loads (10 N, 20 N, 30 N). Sliding distance was 300 m and each experiment was repeated five times. The tests were performed at room temperature. The wear behaviour of the block was monitored in terms of the wear track (scar) width (figure 1). Using the wear track width and geometry of the contact pair, the wear volume (expressed in mm3) was calculated.

3. RESULTS

3.1. Wear

Values of calculated wear volume as function of normal load and sliding speed are shown on figure 2a-c and 2d-f, respectively. It should be noted that in the beginning contact is realised through line contact between block and steel disc, while it exceeds in area contact with development of wear. The increase of the normal load produced increase of wear volume (figures 2a-c), especially pronounced under the lowest sliding speed on this test, 0.25 m/s. The increase of sliding speed produced decrease of wear volume and based on that it can be clearly concluded that the lowest value of wear volume can be achieved under the lowest value of normal load and the highest value of sliding speed. figure 2d confirms previous statement. Mentioned trends are noticeable for all tested materials, both base ZA-27 alloy and nanocomposites reinforced with SiC nanoparticles.

It is noticeable from figure 2 that there is no clear distinction in wear volume values between tested materials. Under the lowest value of sliding speed the lowest value of wear volume exerts base ZA-27 alloy, while in all other cases the lowest value of wear volume exerts nanocomposite with 5 vol.% of SiC nanoparticles.

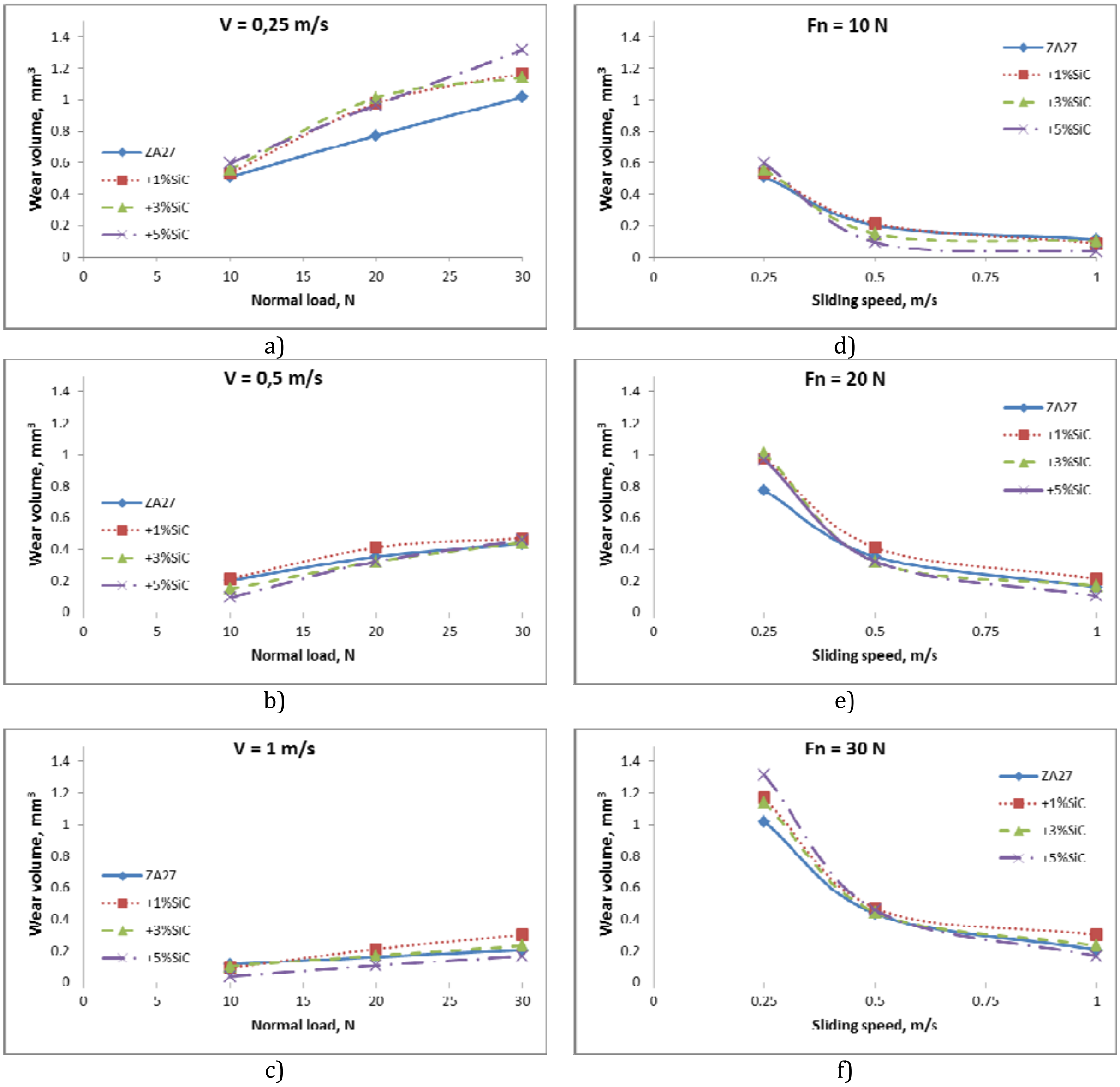


Figure 2. Dependence of wear volume on normal load (a-c) and sliding speed (d-f).

3.2. Friction

Obtained value of coefficient of friction as function of normal load and sliding speed is shown on figure 3a-c and 3d-f, respectively. The increase of the normal load and sliding speed produced increase of coefficient of friction, for all tested materials. The obtained values of coefficient of friction for all tested materials are very close and oscillate in the range from 0.38 to 0.49. Due to that it is impossible to conclude which of the tested materials possess the best frictional properties. Values of coefficient of friction presented in figures 3a-f are steady state values. Also, from presented plots on figure 3 it can be concluded that increase of reinforcement content in base za-27 alloy has no influence on coefficient of friction.

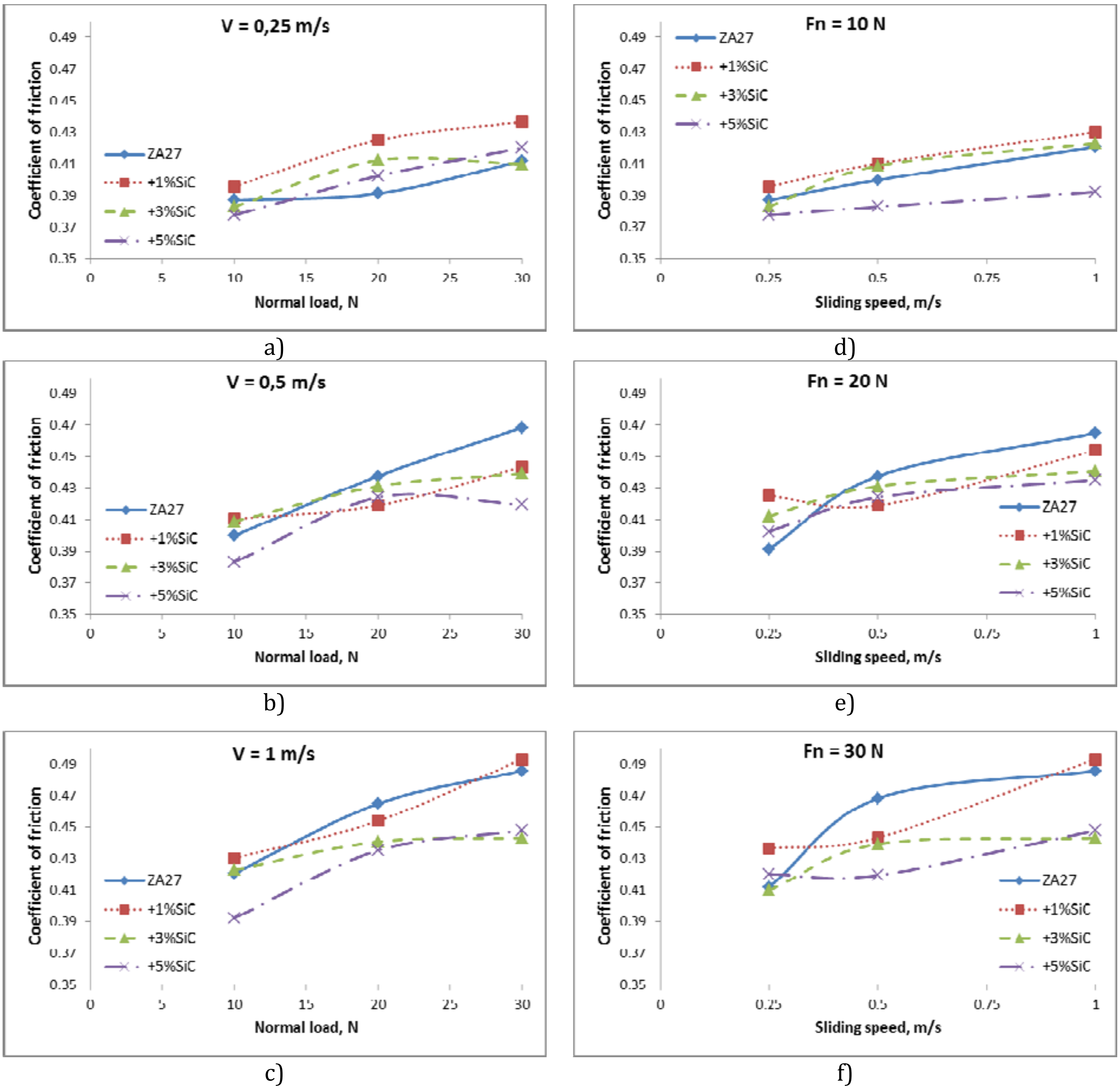
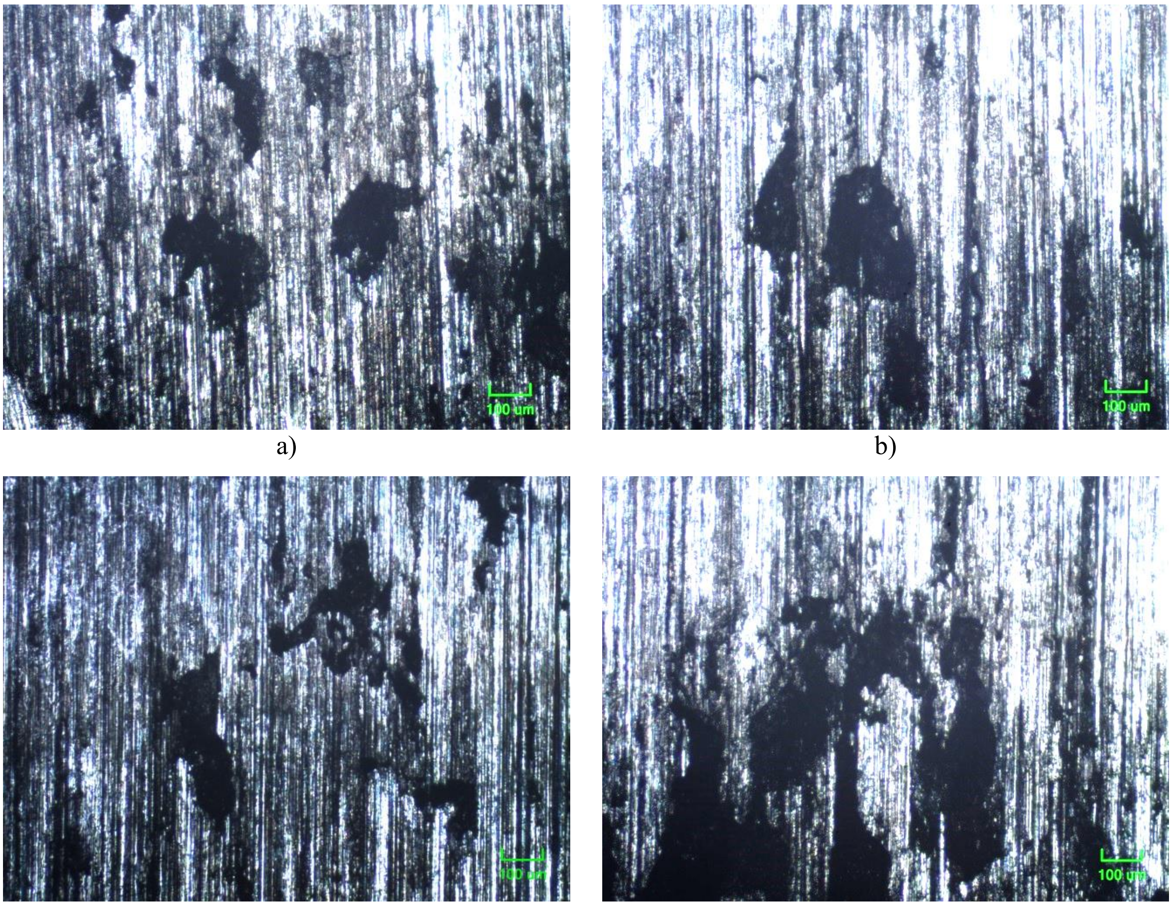


Figure 3. Dependence of coefficient of friction on normal load (a-c) and sliding speed (d-f).

4. DISCUSSION

From presented results it can be clearly noticed that there is no major differences in obtained values of coefficient of friction and wear volume between all tested materials. Based on obtained hardness and density values of tested materials, increase of reinforcement content in base alloy result in decrease of hardness and density of nanocomposites. Decrease of those values indicates on structural irregularities of obtained nanocomposites, such as porosity [25-27] and uneven distribution of nanoparticles in base alloy and formation of an agglomerate of nanoparticles [28-30].

Since the tribological tests were performed without lubrication increase in sliding speed results in increase of contact temperature and based on that oxidation process is pronounced. Decrease of wear volume value with increase of sliding speed indicates that on contact surfaces some kind of tribological layer was generated. Generated oxide layer on contact surfaces protects them and decrease intensity of wear processes.



a) b) c) d)

Figure 4. Wear tracks at 20N and 0.5m/s: a) base ZA-27 alloy, b) 1 vol.% of SiC, c) 3 vol.% of SiC and d) 5 vol.% of SiC.

Analysing optical microscopy images of generated wear tracks on tested materials, both base ZA-27 alloy (figure 4a) and obtained nanocomposites (figure 4b-c) the existence of pits within wear track that are surrounded with parallel grooves can be noticed. Parallel grooves within the wear track indicate that abrasive wear is the dominant wear mechanism while noticed pits are result of fragmentation from generated tribological contact layers. Fragmentation can be result of agglomerated nanoparticles in sub surface layer or a result of fatigue of the contact layer [31]. During fatigue process initial crack is generated in places where agglomerates and pores are present. Due to shear force crack develops until reaching the surface or merging with another crack which results in fragmentation of surface layer.

5. CONCLUSION

Paper presents tribological investigation of nanocomposites based on ZA-27 alloy, reinforced with SiC nanoparticles, with average size of 50 nm. It should be noted that nanocomposites were obtained using compocasting procedure, while the content of SiC particles in the alloy was 1, 3 and 5 vol.%. Conclusions drawn from this experimental work are as follows:

- Increase in volume content of reinforcement results in decrease of density and hardness due to existence of structural irregularities such as porosity and uneven distribution of nanoparticles and their agglomeration.

- Present structural irregularities diminishes positive effects of nanoparticles reinforcement and due to that increase volume content of reinforcement has no influence on wear and frictional properties.
- Wear resistance of all tested materials increases with sliding speed increase as a result of tribological layer generation.
- Dominant wear mechanism was abrasive wear combined with fragmentation of generated tribological surface layer.

ACKNOWLEDGMENTS

Research presented in this paper was supported by Ministry of Education, Science and Technology Development of Republic of Serbia, Grant TR-35021.

REFERENCES

1. Türk, A., Durman, M., Kayali, E., The effect of manganese on the microstructure and mechanical properties of zinc–aluminium based ZA-8 alloy, *J. Mater. Sci.* **42**, 2007, 8298-8305.
2. Türk, A., Kurnaz, C., Şevik, H., Comparison of the wear properties of modified ZA-8 alloys and conventional bearing bronze, *Mater. Des.* **28**, 2007, 1889-1897.
3. Kurnaz, S., Sevik, H., Türk, A., Ozsarac, U., The Effect of Ti–B and Sr on the mechanical behaviour of the Zinc–Aluminum-based ZA-12 alloy produced by gravity casting, *International Journal of Materials Research* **97**, 2006, 1152-1157.
4. Delneuville, P., Tribological behaviour of ZnAl alloys (ZA27) compared with bronze when used as a bearing material with high load and at very low speed, *Wear* **105**, 1985, 283-292.
5. Harmsen, M., Laufer, E., Masounave, J., Si-modified ZA alloy for journal bearing applications, *Wear* **192**, 1996, 128-133.
6. Prasad, B., Patwardhan, A., Yegneswaran, A., Dry sliding wear characteristics of some zinc-aluminium alloys: a comparative study with a conventional bearing bronze at a slow speed, *Wear* **199**, 1996, 142-151.
7. Prasad, B., Yegneswaran, A., Patwardhan, A., Characterization of the wear response of a modified zinc-based alloy vis-à-vis a conventional zinc-based alloy and a bearing bronze at a high sliding speed, *MMTA* **27**, 1996, 3513-3523.
8. Tjong, S., Chen, F., Wear behavior of As-cast ZnAl27/SiC particulate metal-matrix composites under lubricated sliding condition, *Metall and Mat Trans A* **28**, 1997, 1951-1955.
9. Chen, T., Yuan, C., Fu, M., Ma, Y., Li, Y., Hao, Y., In situ silicon particle reinforced ZA-27 composites: Part 1 – Microstructures and tensile properties, *Materials Science and Technology* **24**, 2008, 1321-1332.
10. Li, Y., Ngai, T., Xia, W., Zhang, W., Effects of Mn content on the tribological behaviors of Zn-27% Al-2% Cu alloy, *Wear* **198**, 1996, 129-135.
11. Babic, M., Slobodan, M., Dzunic, D., Jeremic, B., Bobic, I., Tribological Behavior of Composites Based on ZA-27 Alloy Reinforced with Graphite Particles, *Tribol Lett* **37**, 2010, 401-410.
12. Sharma, S., Girish, B., Kamath, R., Satish, B., Graphite particles reinforced ZA-27 alloy composite materials for journal bearing applications, *Wear* **219**, 1998, 162-168.
13. Girish, B., Prakash, K., Satish, B., Jain, P., Prabhakar, P., An investigation into the effects of graphite particles on the damping behavior of ZA-27 alloy composite material, *Mater. Des.* **32**, 2011, 1050-1056.
14. Mishra, S., Biswas, S., Satapathy, A., A study on processing, characterization and erosion wear behavior of silicon carbide particle filled ZA-27 metal matrix composites, *Mater. Des.* **55**, 2014, 958-965.
15. Sharma, S., Girish, B., Somashekar, D., Kamath, R., Satish, B., Mechanical properties and fractography of zircon-particle-reinforced ZA-27 alloy composite materials, *Composites Science and Technology* **59**, 1999, 1805-1812.
16. Bobić, I., Jovanović, M., Ilić, N., Microstructure and strength of ZA-27-based composites reinforced with Al2O3 particles, *Mater Lett* **57**, 2003, 1683-1688.
17. Miroslav, B., Mitrović, S., Zivic, F., Bobić, I., Wear Behavior of Composites Based on ZA-27 Alloy Reinforced by Al2O3 Particles Under Dry Sliding Condition, *Tribol Lett* **38**, 2010, 337-346.
18. Babic, M., Mitrovic, S., Zivic, F., Effects of Al2O3 particle reinforcement on the lubricated sliding wear behavior of ZA-27 alloy composites, *J Mater Sci* **46**, 2011, 6964-6974.
19. Bobić, I., Babić, M., Vencl, A., Bobić, B., Mitrović, S., Artificial aging of thixocast ZA27 alloy and particulate ZA27/SiC p composites, *Int J Mater Res* **104**, 2013, 954-965.

20. Mitrovic, S., Babic, M., Miloradovic, N., Bobic, I., Stojanovic, B., Dzunic, D., Pantic, M., Wear Characteristics of Hybrid Composites Based on Za27 Alloy Reinforced With Silicon Carbide and Graphite Particles, *Tribology in Industry* **36**, 2014, 204-210.
21. Bobic, B., Mitrovic, S., Babic, M., Vencl, A., Bobic, I., Corrosion Behavior of the As-cast and Heat-treated ZA27 Alloy, *Tribology in Industry* **33**, 2011, 87-93.
22. Bobic, B., Vencl, A., Babic, M., Mitrovic, S.,Bobic, I., The Influence of Corrosion on the Microstructure of Thermally Treated ZA27/SiCp Composites, *Tribology in Industry* **36**, 2014, 33-39.
23. Bobic, B., Bobic, I., Vencl, A., Babic, M., Mitrovic, S., Corrosion Behavior of Compocasted ZA27/SiCp Composites in Sodium Chloride Solution, *Tribology in Industry* **38**, 2016, 115-120.
24. Babic, M., Vencl, A., Mitrovic, S., Bobic, I., Influence Of T4 Heat Treatment On Tribological Behavior Of Za27 Alloy Under Lubricated Sliding Condition, *Tribol Lett* **36**, 2009, 125-134.
25. Karbalaei Akbari, M., Baharvandi, H., Mirzaee, O., Nano-sized aluminum oxide reinforced commercial casting A356 alloy matrix: Evaluation of hardness, wear resistance and compressive strength focusing on particle distribution in aluminum matrix, *Composites Part B* **52**, 2013, 262-268.
26. Mazahery, A., Abdizadeh, H., Baharvandi, H., Development of high-performance A356/nano-Al2O3 composites', *Mater. Sci. Eng., A* **518**, 2009, 61-64.
27. Sajjadi, S., Torabi Parizi, M., Ezatpour, H., Sedghi, A., Fabrication of A356 composite reinforced with micro and nano Al2O3 particles by a developed compocasting method and study of its properties, *J. Alloys Compd.* **511**, 2012, 226-231.
28. Ezatpour, H., Sajjadi, S., Sabzevar, M., Huang, Y., Investigation of microstructure and mechanical properties of Al6061-nanocomposite fabricated by stir casting, *Mater. Des.* **55**, 2014, 921-928.
29. Poirier, D., Drew, R., Trudeau, M., Gauvin, R., Fabrication and properties of mechanically milled alumina/aluminum nanocomposites, *Mater. Sci. Eng., A* **527**, 2010, 7605-7614.
30. Khorshid, T. M., Jahromi, S., Moshksar, M., Mechanical properties of tri-modal Al matrix composites reinforced by nano- and submicron-sized Al2O3 particulates developed by wet attrition milling and hot extrusion, *Mater. Des.* **31**, 2010, 3880-3884.
31. Tang, F., Wu, X., Ge, S., Ye, J., Zhu, H., Hagiwara, M., Schoenung, J., Dry sliding friction and wear properties of B4C particulate-reinforced Al-5083 matrix composites, *Wear* **264**, 2008, 555-561.

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Tribological Journal BULTRIB Vol. 7, 2018
Papers from the 13th International Conference **BULTRIB '18**
25-27 October 2018, Sofia, Bulgaria
Society of Bulgarian Tribologists
FIT – Technical University of Sofia

THE ABRASIVE PROPERTIES OF DETONATION NANODIAMONDS

Anna PETROVA, Adelina MITEVA

***Abstract**: A large area in the application of detonation nanodiamonds is surface polishing. Mills, diamond cutting blades, drill bits and blades with embedded diamond particles are used in the various industries, with new metal-diamond connections, resistant to high temperatures and mechanical stress, ensuring a high cutting speed. An important process in the production of details is the finishing of high-precision polishing for the needs of: radio engineering, electronics, optics and mechanical engineering*

***Keywords:** detonation nanodiamonds, abrasive properties, carbon nanostructures, coatings, poloshing*

1. INTRODUCTION

The applications of detonation nanodiamonds (DNDs) are very diverse in industry and science [1-18]. In some applications, the use of untreated detonation nanodiamonds is acceptable - the starting charge, which is almost twice as cheap. DNDs are used to create high quality materials and coatings with nanocrystalline structure and particle size up to 100 nm.

The use of DNDs in polishing surfaces has been proven in science. A small percentage of the addition of particulate matter (oxides, carbides, or borides) in electrochemical coatings provides increased hardness of the composites and reduces the wear of the coatings. This is explained by the finer crystalline structure of the metal coatings. The added particles play the role of crystallization centers. The microhardness of the metal grows in proportion to $d^{(1/2)}$, where d is the size of the crystal. The DNDs in the electroplating bath must be sufficiently dispersed and the particles (in the form of a suspension) distributed as evenly as possible in the volume. Environmental protection is now a vital and global priority, which is also a priority in the coating processes.

Nanoscale diamonds are part of nanomaterials whose production, modification and use are of increasing interest to scientists and engineers. Of the whole variety of nanodiamonds, detonation nanodiamonds are the most interesting in practice.

Their application in the field of composite coatings is determined by the following characteristics:

- the small size of nanodiamond grains (4 ÷ 6 nm) is related to their anomalous properties compared to the properties of other diamonds;
- the particles are a single crystalline nucleus with a spherical shape and a three-layer coating;
- highly developed active surface;
- functional groups on the surface of particles of different composition ($COOH^-$, OH^-, SO_3H^-, NO_3^-, NO_2^-) are formed during the redox process of purification.

2. THEORETICAL CONSIDERATION

Nanocomposites are materials in which the dimensions of the filler particles are in nanometric ranges from 10 to 1000 nm. In recent years, it has become clear that the definition of nanoparticles is far beyond their dimensional characteristics and includes the specificity of the state of matter in the particle sizes in the nanodiamond.

Kadomtsev-Shevchenko's synergistic theory describes the specificity of the condition depending on the size. The nanoworld is obtained by separating the macroworld from the elementary particles. Thus, nanoscale objects have classic properties in complex with quantum effects (new properties). We are looking at nanocomposites, a type of metal designed to produce segments used in stone cutting.

To amplify the effect of the nano-filler, the movement of dislocations is essential. The influence of the size and content of the filler, in this case DNDs, is also significant. These are single crystals with a maximum allowable Mohs hardness value of 10. An approximate qualification can be given to nanoparticles. Particles up to 1000 nm in diameter are thinner, i.e. they do not give a noticeable effect. Strengthening are from 100 to 1000 nm in diameter.. Enhancement of the effect of the filler is obtained by adding particles of size 10 to 100 nm and strengthening - at sizes from 10 to 45 nm.

For DND as filler, the following change is observed depending on the grain diameter d. A decrease in d leads to an increase in the specific surface area S of the diamond powder and a decrease in the pycnometer density ρ.

The advantage of synthetic diamond powders compared to natural ones is the high abrasive ability of sizes smaller than 200 μm, the ability to sharpen and the low financial value.

Depending on the size of the grains, the following is the division of diamond powders:

Grains with grain size 3000 - 60 μm. Grinding powders are divided into fractions by two sieves - they pass through the steam and hold on to the second (for example 60/40). There are methods for sorting by the magnetic, electrical, adsorption and geometric characteristics of grains.

Micropowders with a grain size of 60 to 1 μm. They are used for polishing in pastes and suspensions. The main characteristic of micro-pores for surface treatment is their abrasive ability and roughness.

The sub-micro powders are 1 to 0.1 μm in size and down.

3. SOME APPLICATIONS

In article [1] are discused the nanodiamonds, dynamically synthesized from graphite, represent a promising material for obtaining superhard compacts. Abrasive properties of diamond powders with the nanostructure of grains are better than those of powders of natural and synthetic single crystal diamonds The composite thickness 1-2 mm is suitable for making cutting tools, cylindrical samples with the height and diameter larger than 2-3 and 3-5 mm, respectively, are needed for producing wire drawing dies. The infiltration depth can be increased by the use of diamond powder with a narrow particle size distribution. The authors describe the process of producing bulk superhard ceramics from SiC and dynamicallysynthesized nanodiamonds, as well as their mechanical behavior and microstructure. One of the results of this work is the synthesis of bulk cylindrical samples 2-2.5 mm in height and 3.5 mm in diameter, on the nanodiamond base with a very high hardness of 80 GPa and a Young's modulus of 700 GPa. They suggest that structural defects of the diamond-SiC boundaries account for the discrepancy in the case of a nearly dense composite. The structure fitting diamond-SiC was observed. The SiC structure changes from the nanostructure to submicronstructure in the diamond-SiC direction. [1]

The presence of nanodiamond on the surface of the Ni-ND composite was apparent in [5]. It was not possible to remove ND from the surface in an ultrasonic bath or a nitric acid chemical etching bath. The adhesion of ND to the coating surface is very strong. The nanodiamond agglomerate size on the surface is very small, for some areas lower than 100 nm. Nanodiamond particles of such small sizes located on the surface shouldn't result in harmful abrasive properties of the surface [5].

Shear resistance is expected to be lowered when temperature is increased in [6]. The coefficient of friction could be lowered with decreasing shear resistance. Protective non-sticky coating with nanodiamond ranging from 0 to 4 wt. % was fabricated to investigate the effect of nanodiamond addition on tribological performance. The enhanced tribological properties with the small addition of nanodiamond were achieved by the uniform dispersion of nanosized particles having large specific surface area and excellent properties. The width of wear track and coefficient of friction were reduced significantly by the addition of up to 4 wt. % nanodiamond at both room temperature and 150 ºC. The variation of microstructure due to nanodiamond addition and the transferred layers containing nanodiamond was the main mechanism for the tribological behavior of nanodiamond added PTFE film [6].

A number of unsolved technological and marketing problems that hinder wide applications of detonation nanodiamonds in great quantities have been analyzed in [7]. A proposal has been made that ammunition should be utilized in a closed pool without discharging it and abrasive diamond powders should be synthesized simultaneously with the detonation nanodiamonds by an explosion of a large-weight charge in a heavy shell under water.

Owing to its superior mechanical properties, nanodiamond holds great potential to improve tribological characteristics of composites in [8]. The author reports on the wear and dry friction of epoxy- nanodiamond composites prepared from as-received and aminated nanodiamond across the length scale range from macro to nano. Comparison of macroscale, microscale, and nanoscale frictional behavior shows that nanodiamond is highly effective in improving the wear resistance and friction coefficients of polymer matrices across the different length scales. Both types of nanodiamonds wear resistance and friction coefficients of epoxy-nanodiamond composites were significantly improved, aminated nanodiamond outperformed as-received nanodiamond, which authors account to the formation of a strong interface between aminated nanodiamond and the epoxy matrix. This study also shows that agglomerates within epoxy-nanodiamond composites containing 25 vol. % nanodiamond were able to wear an alumina counterbody, indicating very high hardness and Young's modulus of these agglomerates, that can eventually replace micron sized diamonds currently used in industrial abrasive applications [8].

Friction accounts for a large amount of energy lost in mechanical systems and applications [9]. Nanofluids, with particles less than 100 nm, added to a base fluid have been proven to be effective in reducing friction and wear. Diamond has superior mechanical, thermal, optical, electrical, and chemical properties. Nanodiamond holds a lot of promise for use in nanofluids. The tribological properties of oil-based nanofluids with spherical nanodiamond particles with the size of 3-10 nm in diameter were investigated using a ball-on-disk friction test by varying nanodiamond concentration, sliding velocity, normal load, and disk roughness. The friction testing was performed from authors using a UMT-2 Micro Tribometer and wear analysis was performed and chemical composition of the disk surface was examined using a WYKO 3D surface profiler with X-ray photoelectron spectroscopy. The addition of nanodiamonds to oil leads to a reduction in the coefficient of friction but an increase in wear of the disk. [9].

To improve W. Miao et all. the oxidation resistance of ultrafine diamonds and broaden their applications in the field of ultra-precision grinding, titania-coated UFDs were prepared successfully with the aid of acetic acid and polyvinylpyrrolidone (PVP). Compared with the pristine UFDs, the oxidation resistance temperature of titania-coated UFDs was enhanced by around 130 ºC. The titania shell thickness was approximately 4 nm. They disscus that titania-coated UFD-vitrified bond wheels were manufactured through the titania-coated UFD-vitrified bond composite powders obtained by a polyacrylamide gel (P-G) method, with which their mechanical performances were largely improved. These results in [10] provide a new pathway of manufacturing high-quality ultra-precision grinding wheels.

The results of polishing, using suspensions of nanodiamonds produced by detonation synthesis at different plants, of the surfaces of 23 solid materials having different chemical compositions, production processes, structure, electronic properties, hardness, reactivity, and application are described are presents in [11]. AFM technique is used to compare the roughness of these surfaces with the surfaces of such materials subjected to polishing with diamond synthetic micropowders (of grades 1/0, 0.25/0, 0.1/0) and to chemical-mechanical polishing (CMP) with amorphous colloid silica. Stable nanodiamond suspensions are shown to cause a number of effects, namely, polishing, scratching, plastic flow of surface layers, and CMP. The aggregative state of solid particles is shown to be of importance. Polishing with NDs is found to be accompanied by mechanical nanoscratching, which can be leveled by the introduction of certain etchants into an ND suspension. The author use of amorphous nanoparticles is the only technique that does not induce deformation in the surface layer of a material [11].

The mechanical properties of epoxy-based nanocomposites reinforced by nanodiamond particles were investigated in [12]. The results showed that while the addition of 0.1 wt % of ND improved the Young's modulus and tensile strength compared with those of the pure epoxy, the mode I fracture toughness did not show any improvement. The effect of shear deformation on fracture properties of nanocomposites, mixed mode fracture resistance of nanocomposites was investigated. [11], polymer-based nanocomposites [13] was found that as the share of shear deformation in mixed mode loading increases, the positive effect of ND particles enhances. By many authors nanodiamonds have attracted considerable attention in several engineering fields such as biological systems, abrasive pastes and suspensions for high precision polishing [11], polymer-based nanocomposites [13], wear-resistant surface coatings, cooling fluids, lubricants, and electroplating baths [14]. Few research studies have been performed to investigate the mechanical properties of nanocomposites reinforced by nanodiamonds. Ekimov and Gromnitskaya [1] reported 4.6 % and 11.6 % improvements in the tensile strength and Young's modulus of nanocomposites reinforced with 3 wt % of ND.

The boundary between technical diamonds and diamonds suitable for jewelry production is very approximate and depends on the specific conditions of rejection of the extracted stones. Some types of particularly responsible tools use diamond jewelry. Synthetic diamonds are mainly used for technical purposes.

The main applications of diamonds are given in the form of tables (see table 1 and table 2). Depending on the quality and purpose, industrial diamonds can be divided into the following groups:

1) Diamonds processed to obtain grains of a certain geometric shape. These include diamonds intended for the manufacture of cutters, drills, tips, glass cutters, bearings, etc.;
2) Diamond crystals used in raw form in drill bits, diamond-metal pencils, etc.;
3) Abrasive diamonds - mainly small crystals having significant defects (cracks, inclusions, voids) and suitable only for grinding into powder.

"Atelier Jacques Dembitzer" company produces diamond tools from single crystals and crushed diamonds. Diamonds and diamond tools made in Belgium are exported mainly to the USA, Great Britain, France and Germany.

Table 1. Two types of diamonds

Diamonds	
Technical diamonds	*Jewelry diamonds*

Table 2. Three main types of technical diamonds

Technical diamonds		
I.	*II.*	*III.*
- typeable diamonds	*- abrasive diamonds, powders*	*- drilling tool*
- incisors	*- grinding wheels*	*- diamond metal pencils*
- dies	*- cutting discs*	*- straightening diamonds*
- contacts	*- lapping*	*- glass cutters*
- drill	*- paste*	*- contacts*
- bearings	*- drill bits*	
- (faceted) glass cutters	*- diamond metal pencils*	
- circle edging diamonds	*- polishing powders*	
- hardness tips	*- denture tool*	
- surface cleanliness tips		

Large enterprises for the production of diamond tools are also organized in the USA, Israel and Germany.

The United States is the main consumer of industrial diamonds in the capitalist world and the largest consumer of diamond tools. Diamond tool manufacturing company engaged in "Norton Company" and "Korborundum" with the enterprise, not only in the USA but in the UK, France, South Africa, Australia and Canada, and producing almost all kinds of diamond tools.

Consumption of industrial diamonds in the USA over the past decades has been growing steadily. So, it amounted to (in million carats): 1955 - 11; 1960 - 13.5; 1965-15; 1970 - 21; 1974-1975 - 25-26. At the same time, the use of diamonds for various technical needs is approximately: grinding, sharpening and finishing of tools and machine parts from hard alloys 60-70 %; grinding wheel mandrel 10-12 %; diamond drilling 10 %; wire drawing 10 %; cutting and grinding of parts and products made of glass, ceramics, marble, drilling and finishing of carbide parts, processing of watch and jewelry 10-12 %. Since 1975, accurate USA diamond consumption data has not been published.

The largest consumers of diamonds in Western Europe are the United Kingdom, Belgium, Germany, France, Italy, Sweden and Switzerland [15].

4. CONCLUSION

It turned out that detonation nanodiamonds have a number of unusual properties. Recent studies have shown that nanodiamonds can be used to create nanocomposite materials, elements of nanoelectronics, selective adsorbents and catalysts, and objects of biomedical use.

The most advanced application area of nanodiamonds is polishing compounds. The abrasive properties of DNDs are the most applicable properties of DNDs up to now.

REFERENCES

1. Ekimov, E. A., E. L. Gromnitskaya, S. Gierlotka, W. Lojkowski, B. Palosz, A. Swiderska-Sroda, J. A. Kozubowski, A. M. Naletov, Mechanical behavior and microstructure of nanodiamond-based composite materials, J. of materials science letters, 21, 2002, pp. 1699-1702.
2. Kandeva, M., Zh. Kalitchin, P. Svoboda, S. Sovilj-Nikic, General Methodology for Studying the Tribological Processes on the Basis of the Communicative Potential, Journal of the Balkan Tribological Association, 25, 2019, pp. 432-442.

3. Kandeva, M., P. Svoboda, Zh. Kalitchin, T. Penyashki, G. Kostadinov, Wear of Gas-Flame Composite Coatings with Tungsten and Nickel Matrix. Part I. Abrasive Wear, Journal of Environmental Protection and Ecology, 20, 2019, pp. 811-822.
4. Кандева-Иванова, М., Контактният подход в инженерната трибология, ТУ-София, 2012.
5. Petrov, I., P. Detkov, A. Drovosekov, M. V. Ivanov, T. Tyler, O. Shenderova, N. P. Voznecova, Y. P. Toporov, D. Schulz, Nickel galvanic coatings co-deposited with fractions of detonation nanodiamond, Diamond and Related Materials, Volume 15, Issues 11-12, 2006, pp. 2035-2038.
6. Lee, Jung-Yeob, Dae-Soon Lim, Tribological behavior of PTFE film with nanodiamond, Surface and Coatings Technology, Volumes 188-189, 2004, pp. 534-538.
7. Danilenko, V. V., Nanodiamonds: Problems and prospects, Journal of Superhard Materials, Volume 32, Issue 5, 2010, pp 301-310.
8. Neitzel, I., V. Mochalin, J. A. Bares, R. W. Carpick, A. Erdemir, Y. Gogotsi, Tribological Properties of Nanodiamond-Epoxy Composites, Tribology Letters, Volume 47, Issue 2, 2012, pp. 195-202.
9. Caymen Novak, David Kingman, Kyle Stern, Qian Zou & Luan Gara, 2014, Tribological Properties of Paraffinic Oil with Nanodiamond Particles, J. Tribology Transactions, Volume 57, 2014, Issue 5, Pages 831-837.
10. Weipeng Miao, Ning Yan, Yucheng Zhao, Mingyao Liu, Yapeng Li, Liping Wang, Qin Zou, Hu Tang, Lina Qiao, Mingzhi Wang, 2016, Synthesis and application of titania-coated ultrafine diamond abrasive particles, Ceramics International, Volume 42, Issue 7, pp. 8884-8890.
11. A. S. Artemov, 2004, Polishing nanodiamonds, Physics of the Solid State, Volume 46, Issue 4, pp. 687-695.
12. Ayatollahi, M. R., E. Alishahi, S. Shadlou, Mechanical Behavior of Nanodiamond/Epoxy Nanocomposites, International Journal of Fracture, Volume 170, Issue 1, 2011, pp. 95-100.
13. Kuznetsov, V., Lipa, S., Nanodiamond and onion-like carbon polymer nanocomposites. Diamond and Related Materials 16, 2007,1213-1217.
14. Dolmatov, V. Y., Detonation synthesis ultradispersed diamond: properties and applications. Russian Chemical Reviews 70, 2001, 607-626.
15. Васильев, Л. А., Белых, З. П., Алмазы, их свойства и применение, http://iznedr.ru/books/item/f00/s00/z0000035/st019.shtml

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Tribological Journal BULTRIB Vol. 7, 2018
Papers from the 13th International Conference **BULTRIB '18**
25-27 October 2018, Sofia, Bulgaria
Society of Bulgarian Tribologists
FIT – Technical University of Sofia

DETONATION NANODIAMONDS - SOME BIOMEDICAL APPLICATIONS

Adelina MITEVA, Anna PETROVA

Abstract: *Nowadays investigations of detonation nanodiamonds are the subject of great interest. This is mainly due to their unique properties and consequently to their actual and potential applications in various fields of industry and everyday life. In this paper we briefly review some of the main existing medical and biological applications of detonation nanodiamonds. Possible future extensions of these biomedical applications are considered.*
Keywords: *detonation nanodiamonds, biomedical applications, carbon nanostructures, drug delivery system, nanomedicine*

1. INTRODUCTION

Nanodiamonds (NDs) have attracted a great deal of interest, scientific and technological, due to their unique properties - electronic, structural, thermal, chemical, biological, mechanical, and optical [1-43]. NDs properties make them suitable for numerous actual and potential applications in various fields of industry and life [1-13]. Among all nowadays obtained nanodiamonds the most suitable as novel nanomaterials for biomedical applications are the detonation nanodiamonds (DNDs) or the detonation nanodiamond powders [1,3,6,7,9,12,14,25]. This is due to superior DNDs properties such as: low size dispersion - the bulk of all particles are 4 to 5 nanometers in size; stable inert core; reactive surface; ability to form hydrogels; facile surface functionalization including bio-conjugation; versatile functionalization; large surface area; high adsorption capacity; inertness in relation to the environment of the digestive tract.; as well as high biocompatibility. We can see in the available literature the growing interest in DNDs as numerous: patents [14-22]; review papers [28,30,35-40,42]; books [6,7,9,12,13,25]; companies, which produce and sell nanodiamonds (Nanostructured and Amorphous Materials, Inc, (USA); YTM ARGE A.S. (Istanbul, Turkey); Beijing Grish Hitech Co. (China); etc.).

In this paper we will briefly present several biomedical applications of DNDs, namely some of the most useful and attractive.

Here we will only look at detonation nanodiamonds (DNDs): diamonds that are nanoscopic particles of diamond, fabricated by detonation (DND) or high-temperature high-pressure (HPHT) methods.

2. EXAMPLES OF SOME APPLICATIONS

Nanodiamonds have attracted considerable attention in recent years in different research biomedical areas such as biological sensing, medical therapy, fluorescent markers, enzyme immobilization and so on [1].

In article [19] are discussed the main characteristics of the DNDs, with their potential use in stimulation, indication and monitoring of the wastewater treatment and biodegradation processes. The effect of diamond nanoparticles on the transformation of the azo-dye amaranth during the treatment process, modeled in sandy sequencing batch biofilter has been discussed as case study. In the described examples key parameters were evaluated: residual concentration of amaranth, enzyme activities, effectiveness of amaranth decolorization, chemical oxygen demand and total organic carbon. The data showed the positive role of the diamond nanoparticles as a modulator. These results discover perspectives for further research and potential applications of DNDs in the stimulating of biodegradation processes in wastewater treatment technologies.

The paper [20] discusses the prospects for using modified detonation nanodiamonds with novel properties as a new promising material for the development of nanotechnologies intended for biological and medical purposes. The authors report that nanodiamonds synthesized by detonation can be used to further purify commercial protein preparations and that enzymes adsorbed on diamond nanoparticles retain their activity. The paper presents results of in vivo experiments with nanodiamonds administered to animals via different routes.

In the review [28] authors presented recent studies on carbon nanomaterials for biological applications revealed that carbon nanodiamonds are much more biocompatible than most other carbon nanomaterials, including carbon blacks, fullerenes and carbon nanotubes. The noncytotoxic nature of nanodiamonds, together with their unique strong and stable photoluminescence, tiny size, large specific surface area and ease with which they can be functionalized with biomolecules, makes nanodiamonds attractive for various biomedical applications both in vitro and in vivo. In this article, we present some of the important issues concerning the synthesis and surface functionalization of diamond nanoparticles for nanomedicine as well as an overview of the recent progress in this exciting field by focusing on the potential use of nanodiamonds and their derivatives for single particle imaging in cells, drug delivery, protein separation and biosensing.

During the last decade, ND has furthered its way into the biomedical field, due mainly to its inherent photoluminescent properties [30]. In parallel, the development of advanced biomedical imaging methods and techniques have faced a steep upswing, making these two a ‘perfect match’. The optical and physical properties of ND can be tuned, rendering them highly interesting as versatile biomedical imaging probes. In the short review [30], authors cover a few of the most recently emerged applications of ND in biomedical imaging and contemplate on current challenges and future directions.

DLC (Diamond Like Carbon) films are used in many applications, and nanoparticles are being used as dopant materials in a large number of films. In the investigation [29], DLC films doped with nanodiamond were deposited on Ti_6Al_4V substrates. Detonation nanodiamond was stirred in hexane with a sonicator at 750 W to obtain a suspension, which was introduced by an evaporation process into a PECVD reactor to produce DLC films continuously doped with nanoparticles. An amorphous silicon interlayer was used before depositing the DLC on the Ti_6Al_4V substrate. Raman spectroscopy results showed films with hydrogen contents around 22 %. A scratch test on the Ti_6Al_4V alloy showed critical loads close to 19 N, and corrosion resistance measured via potentiodynamic polarization was improved with doped DLC over that of the bare substrate. An antibacterial test was carried out with Gram-negative Escherichia coli, showing antibacterial activity close to 95 % 6 hours after direct contact with the film. This result suggested that DLC is an excellent material for biomedical purposes. After 18 hours of direct contact with the doped DLC film, antibacterial activity close to 25 % was observed, which suggested that nanodiamonds [29] are able to maintain their antibacterial properties and produce damage to Escherichia coli cells.

In vitro studies [31] of macrophages exposed to micro-sized diamond powder have shown that it does not affect cell viability for at least 30 hours and does not activate or alter cellular morphology. The use of nanodiamonds, alone or attached to small molecules, is used in drugs in various fields such as oncology, cardiology, gastroenterology and dermatology.

Nano-diamonds have been found to accelerate the initial detoxification phase, causing cells to synthesize more and more active enzymes [32].

The effectiveness of modified nanodiamonds (NDs) for the adsorption of mycotoxins, aflatoxin B1 (AfB1) and ochratoxin A (OTA), are investigated in the paper [33]. Binding and release mechanisms of the mycotoxins were addressed using an assortment of NDs modified by different surface treatments, including carboxylation, hydrogenation and hydroxylation, followed by isolating NDs of different sizes. Results indicate that AfB1 adsorption on NDs is directly related to aggregate size, whereas OTA adsorption is primarily centered upon electrostatic interactions that depend on the types of surface functional groups on the ND. Findings show that modified NDs with small aggregation sizes (40 nm) have greater adsorption capacities for AfB1 than yeast cells walls and untreated NDs from various vendors, but comparable to activated charcoal. In OTA studies, positively charged NDs outperformed clay minerals, which are well-known and efficient sorbents for mycotoxins. Furthermore, ND adsorption capacities can be preserved in a wide range of pH.

Due to the inertness of nanodiamond particles, their small size and surface structure, they are well - suited for biological applications, such as labelling and drug delivery [34]. In [34] were discussed the surface structure and functionalisation of diamond nanoparticles. Non - covalent as well as covalent grafting of bioactive moieties is possible, and first applications of fluorescent diamond nanoparticles are described.

Nanodiamonds (NDs) are members of the diverse structural family of nanocarbons that includes many varieties based on synthesis conditions, post-synthesis processes, and modifications. First studied in detail beginning in the 1960s in Russia, NDs have now gained world-wide attention due to their inexpensive large-scale synthesis based on the detonation of carbon-containing explosives, small primary particle size (4 to 5 nm) with narrow size distribution, facile surface functionalization including bio-conjugation, as well as high biocompatibility. It is anticipated [35] that the attractive properties of NDs will be exploited for the development of therapeutic agents for diagnostic probes, delivery vehicles, gene therapy, anti-viral and anti-bacterial treatments, tissue scaffolds, and novel medical devices such as nanorobots. Additionally, biotechnology applications have shown the prospective use of NDs for bioanalytical purposes, such as protein purification or fluorescent biolabeling. The review [35] critically examines the use of NDs for biomedical applications based on type (i.e., high-pressure high-temperature [HPHT], CVD diamond, detonation ND [DND]), post-synthesis processing and modifications, and resultant properties including bio-interfacing. The discussion focuses on nanodiamond material in the form of nanoparticles, while the biomedical uses of nanodiamond coatings and thin films are discussed rather briefly. Specific use of NDs in both non-conjugated and conjugated forms as enterosorbents or solid phase carriers for small molecules including lysozyme, vaccines, and drugs is also considered. The use of NDs as human anti-cancer agents and in health care products is already showing promising results for further development. The review [35] concludes with a look to the future directions and challenges involved in maximizing the potential of these exciting little carbon-based gems in the fields of engineering, medicine, and biotechnology.

In [36] diamond has been considered for use in several medical applications and methods for preparing synthetic diamond surfaces and particles are also described. In addition, developments involving the use of diamond in prostheses, sensing, imaging, and drug delivery applications are reviewed. These developments suggest that diamond-containing structures will provide significant improvements in the diagnosis and treatment of medical conditions over the coming years.

The results in [36] have demonstrated the use of diamond in a variety of medical applications, including drug delivery devices, microelectromechanical devices, and cardiovascular devices. However, several challenges for diamond-based materials and devices must be overcome. Reproducible, scalable processes must be developed to facilitate the translation of diamond coatings to clinical use. The short-term toxicity, long-term toxicity, and fate of diamond, impurities, and breakdown products must be carefully considered using medical application-specific parameters. Additional work is also necessary to optimize the properties of diamond for particular medical applications. Efforts are underway to increase the density of nitrogen-vacancy point defects in small (< 5 nm) nanodiamond particles; for example, Smith et al. ([28,76] in [36]) prepared nanodiamond particles containing nitrogen-vacancy point defects by means of high-energy (2.5 MeV) proton irradiation and thermal annealing. The relationships between biological functionality, surface functionalization, purity, and physical properties (e.g., aspect ratio) must also be carefully considered. Furthermore, improved methods for conjugating pharmacologic agents and biological molecules to diamond must be developed. If these hurdles are overcome, diamond-based materials and devices may be translated to use in medical devices, drug delivery, and medical diagnostic applications over the next few decades.

The review [37] focuses on the selective targeting of NDs for biomedical and biophysical applications from the viewpoint of ND surface functionalizations and modifications. These pretreatments make possible the specific targeting of biomolecules of interest on or in a cell by NDs via a designed biochemical route. The surface of NDs is covalently or noncovalently modified with silica, polymers, or biomolecules to reshape them, control their size, and enhance the colloidal stability and biomolecular selectivity toward the biomolecules of interest. Electroporation, chemical treatment, injection, or endocytosis are the methods generally adopted to introduce NDs into living cells. The pathway, efficiency, and the cell viability depend on the selected method.

General significance from [37]: In the biomedical field, the surface modification facilitates specific delivery of a drug, leading to a higher therapeutic efficacy. In biophysical applications, the surface modification paves the way for the accurate measurement of physical parameters to gain a better understanding of various cell functions.

Nanodiamonds (NDs) are emerging as a promising platform for theranostic particles because they unite a spectrum of important properties into a single agent, including facile synthesis, small size, inertness, rich surface functional groups, biocompatibility, stable fluorescence and long fluorescence lifetime. These unique properties have stimulated the application of NDs in cancer treament and imaging [38]. The majority of these applications rely on the rational engineering of the particle surface, as the surface plays a critical role in carrying bioactive molecules, resisting aggregation and constructing composite materials. In the review [38], recent developments of functionalising NDs for cancer treatment and imaging purposes are discussed. A brief introduction in the structure of NDs and properties of NDs was given, followed by a summary of various surface functionalisation methods. The latter part was organised in three subsections: NDs coated with bioactive compounds, NDs coated with synthetic polymers and NDs/inorganic composites.

Finely divided carbon particles, including charcoal, lampblack, and diamond particles, have been used for ornamental and official tattoos since ancient times. With the recent development in nanoscience and nanotechnology, carbon-based nanomaterials (e.g., fullerenes, nanotubes, nanodiamonds) attract a great deal of interest. Owing to their low chemical reactivity and unique physical properties, nanodiamonds could be useful in a variety of biological applications such as carriers for drugs, genes, or proteins; novel imaging techniques; coatings for implantable materials; and biosensors and biomedical nanorobots. Therefore, it is essential to ascertain the possible hazards of nanodiamonds to humans and other biological systems. In [39] was for the first time, assessed the cytotoxicity of nanodiamonds ranging in size from 2 to 10 nm. Assays of cell viability such as mitochondrial function (MTT) and luminescent ATP production showed [39] that nanodiamonds were not toxic to a variety of cell types. Furthermore, nanodiamonds did not produce significant reactive oxygen species. Cells can grow on nanodiamond-coated substrates without morphological changes compared to controls. These results [39] suggest that nanodiamonds could be ideal for many biological applications in a diverse range of cell types.

The unique combination of properties that nanodiamond provides, are the distinct parameters that render nanodiamond superior to any other nanomaterial when it comes to biomedical applications. The most exciting recent results have been related to the use of nanodiamonds for drug delivery and diagnostics - two components of a quickly growing area of biomedical research dubbed theranostics. However, nanodiamond offers much more in addition [40]: it can be used to produce biodegradable bone surgery devices, tissue engineering scaffolds, kill drug resistant microbes, help us to fight viruses, and deliver genetic material into cell nucleus. All these exciting opportunities require an in-depth understanding of nanodiamond. The review [40] covers the recent progress as well as general trends in biomedical applications of nanodiamond, and underlines the importance of purification, characterization, and rational modification of this nanomaterial when designing nanodiamond based theranostic platforms.

The plasma polymerization of the well known hexamethyldisiloxane monomer was used [41] for deposition of PPHMDS layers with excellent adhesion on different substrates and remarkable properties. For the first time in [41], composites of the type DNDs/PPHMDS were obtained and precisely characterized by different physicochemical methods. The most important result of the study [41] is that by varying DNDs particles type, it is possible to alter the morphological and chemical nature, as well as the biological performance of the resultant composite layers. The treatment of composites surface by ammonia plasma reduce its surface hydrophobisity.

The cytotoxicity test [41] indicates that the cells survive and also grow well in presence of DNDs. The biological studies performed under short term cultures of osteoblast-like MG63 cells proved that on the plain surface of Si-DND/PPHMDS composite, the number of the attached cells is the highest. FN pre-coating improved the celular interaction to all surface, but the cell adhered more readily on Ag-DND/PPHMDS. The same effect was observed after treatment by ammonia plasma.

Multi-color fluorescent nanodiamonds (FNDs) containing a variety of color centers are promising fluorescent markers for biomedical applications (in order to analyze complex biological processes, as well as to track and localize individual drugs, proteins, nucleic acids, and small molecules). Compared to colloidal quantum dots and organic dyes, FNDs have the advantage of lower toxicity, exceptional chemical stability, and better photostability. They can be surface functionalized by techniques similar to those used for other nanoparticles. They exhibit a variety of emission wavelengths from visible to near infrared, with narrow or broad bandwidths depending on their color centers. In addition, some color centers can detect changes in magnetic fields, electric fields, and temperature. In the review article [42], are discussed the current trends in FND's development, including comparison to the early development of quantum dots. In [42] were also highlighted some of the latest advances in fabrication, as well as demonstrations of their use in bioimaging and biosensing.

3. CONCLUSION

NDs are widely used as nanomaterials for biomedical applications, especially in drug delivery and imaging systems. They exhibit remarkable luminescence properties with emission of great stability and of high quantum yield which originate from color centers, as Nitrogen-Vacancy centers emitting in far-red/near infrared, perfectly adapted for biological labeling [8].

The main applications of NDs include its use as a carrier for biologically active substances, biomarkers, biosensors, high efficiency adsorbents, coatings for surgical instruments, cosmetic compositions, UV screening creams and additives for dental materials [43].

Interest in nanodiamonds is great all over the world. But widespread adoption is hindered by a number of problems: lack of standardization of nanodiamonds; low quality stability of nanodiamonds from various manufacturers; immaturity of technology; lack of experience with nanodiamonds; etc.

However, the unique properties of nanodiamonds guarantee their presence in the arsenal of innovative technologies. And unresolved problems enable scientists to apply their creative potential.

Undoubtedly, the study of NDs properties will continue. The main areas of application of DNDs may not yet be completely found, but we have reason to believe that NDs can be used virtually everywhere, and especially in high innovative technology [3].

REFERENCES

1. Даниленко, В. В., Детонационные наноалмазы: проблемы и перспективы, Сверхтвердые материалы, № 5, 2010, 15-28.
2. Nunn, N., M. Torelli, G. McGuire, O. Shenderova, Nanodiamond: A high impact nanomaterial, Current Opinion in Solid State and Materials Science 21, 2017, 1–9.
3. Долматов, В. Ю.,Ультрадисперсные алмазы детонационного синтеза: свойства и применение, Успехи химии, 70, 2001, 687-708.
4. Ho, Dean, ed. Nanodiamonds: applications in biology and nanoscale medicine. Springer Science & Business Media, 2009.
5. Aleksenskiy, A., Baidakova, M., Osipov, V., The fundamental properties and characteristics of nanodiamonds. In Nanodiamonds, Springer, Boston, MA., 2010, 55-77.
6. Долматов, В. Ю., Ультрадисперсные алмазы детонационного синтеза: Получение, свойства, применение, Изд-во СПбГПУ, 2003, 344 с.
7. Витязь, П., Ильющенко, А., Жорник, В., Наноалмазы детонационного синтеза: получение и применение. Минск, Беларус, 2013, 381 с.
8. Martel-Estrada, S. A., Recent progress in biomedical applications of nanodiamonds. Instituto de Arquitectura Diseño y Arte, Nanoscience and Nanotechnology, 8, 2018, 11-24.
9. Верещагин, А. Л., Свойства детонационных наноалмазов, Из-во Алт. гос. техн. ун-та, Барнаул, 2005.
10. Mochalin, Vadym N., Olga Shenderova, Dean Ho, and Yury Gogotsi, The properties and applications of nanodiamonds, Nature nanotechnology 7(1), 2011, 11-23.
11. Kandeva M., V. Kamburov, E. Zadorozhnaya, Zh. Kalitchin, Abrasion Wear of Electroless Nickel Composite Coatings Modified with Boron Nitride Nanoparticles, Journal of Environmental Protection and Ecology, 19, 2018, 1690-1703.
12. Кандева-Иванова М., Контактният подход в инженерната трибология, ТУ-София, 2012.
13. Williams, O. A., ed. Nanodiamond, Royal Society of Chemistry, 2014.
14. Долматов, В. Ю., В. А. Марчуков, В. Г. Сущев, М. В. Веретенникова, Способ получения стабильной суспензии детонационных наноалмазов, Патент RU 2384524 C2.
15. Ставрев, С. Я., Метод за получаване на диамантни монокристали, Патент BG 61132 B1.
16. Ставрев, С. Я., Метод за синтез на нова фаза на въглерода, Патент BG 64040 B1.
17. Долматов, В. Ю., Наноалмаз и способ его получения, Патент RU 2 348 580 C1.
18. Патент-UA-42465-U, Способ профилактики лучевой болезни.
19. Патент-UA-99929-C2, Лечение гепатита цирроза.
20. Патент UA-99928-C2, Способ коррекции алкогольных повреждений печени.
21. Khabashesku, V. N., Y. Liu, N. J. Halas, Fluorinated nanodiamond as a precursor for solid substrate surface coating using wet chemistry, US7858186B2 United States Patent.
22. Han, C. C., Chang, H. C., Lee, S. C., Chen, W.H., Academia Sinica, 2008. Clinical applications of crystalline diamond particles. U. S. Patent 7,326,837.
23. Keremidarska, M., A. Ganeva, D. Mitev, T. Hikov, R. Presker, L. Pramatarova, N. Krasteva, Comparative study of cytotoxicity of detonation nanodiamond particles with an osteosarcoma cell line and primary mesenchymal stem cells. Biotechnology & Biotechnological Equipment, 28, 2014, 733-739.
24. Detonation nanodiamonds and related materials - Bibliography Index, second issue, Eds.: A. Vul, V. Dolmatov, D. M. Gruen, O. Shenderova, St. Petersburg, 2006.
25. Shenderova, O. ed., 2014. Detonation nanodiamonds: science and applications. CRC Press.
26. Yotinov I., M. Belouhova, I. Schneider, Y. Topalova, Application of Nanodiamonds in Wastewater Treatment Technologies, Ecological Engineering and Environment Protection, No 1, 2014, 50-61.
27. Puzyr, A. P., A. V. Baron, K. V. Purtov, E. V. Bortnikov, N. N. Skobelev, O. A. Mogilnaya, and V. S. Bondar, Nanodiamonds with novel properties: a biological study, Diamond and Related materials 16, №12, 2007, 2124-2128.
28. Xing, Y., Dai, L., Nanodiamonds for nanomedicine, Nanomedicine, vol. 4, №2, 2009.
29. Conceição, K., V. M. de Andrade, V. J. Trava-Airoldi, G. Capote, High antibacterial properties of DLC film doped with nanodiamond. Surface and Coatings Technology, 375, 2019, 395-401.
30. Prabhakar, N., Rosenholm, J. M., Nanodiamonds for advanced optical bioimaging and beyond. Current Opinion in Colloid & Interface Science, 2019.

31. Donaldson, K., Stone, V., Tran, C. L., Kreyling, W. and Borm, P. J., Nanotoxicology, 61(9), 2004, 727-728.
32. Belouhova M., Y. Topalova, Influenceof nanodiamonds on key enzyme activities of transformation of azo-dyes amaranth in model sand biofilters, Proceedings International Conference “Ecology-Interdisciplinary Science and Practice”, Part B, 2012, 461-468.
33. Gibson, N. M., T. J. M. Luo, D. W. Brenner, O. Shenderova, Immobilization of mycotoxins on modified nanodiamond substrates, Biointerphases 6, №4, 2011, 210-217.
34. Krueger, A., New carbon materials: biological applications of functionalized nanodiamond materials, Chemistry–A European Journal 14, №5, 2008, 1382-1390.
35. Schrand, A. M., Hens, S. A. C., Shenderova, O. A., Nanodiamond particles: properties and perspectives for bioapplications. Critical reviews in solid state and materials sciences, 34(1-2), 2009, 18-74.
36. Narayan, R. J., Boehm, R. D., Sumant, A.V., Medical applications of diamond particles & surfaces. Materials today, 14(4), 2011, 154-163.
37. Terada, D., Genjo, T., Segawa, T. F., Igarashi, R., Shirakawa, M., Nanodiamonds for bioapplications–specific targeting strategies. Biochimica et Biophysica Acta (BBA)-General Subjects. 2019.
38. Lai, H., Stenzel, M. H., Xiao, P., Surface engineering and applications of nanodiamonds in cancer treatment and imaging. International Materials Reviews, 2019, 1-37.
39. Schrand, A. M., Huang, H., Carlson, C., Schlager, J. J., Ōsawa, E., Hussain, S. M., Dai, L., Are diamond nanoparticles cytotoxic?, The journal of physical chemistry B, 111(1), 2007, 2-7.
40. Turcheniuk, K., Mochalin, V. N., Biomedical applications of nanodiamond, Nanotechnology, 28(25), 2017, 252001.
41. Pramatarova, L., E. Radeva, E. Pecheva, T. Hikov, N. Krasteva, R. Dimitrova, D. Mitev, P. Montgomery, R. Sammons, G. Altankov, The Advantages of Polymer Composites with Detonation Nanodiamond Particles for Medical Applications, In book: On Biomimetics Edition: 2011.
42. Alkahtani, M. H., Alghannam, F., Jiang, L., Almethen, A., Rampersaud, A. A., Brick, R., Gomes, C. L., Scully, M. O., Hemmer, P. R., Fluorescent nanodiamonds: past, present, and future, Nanophotonics, 7(8), 2018, 1423-1453.
43. Yakovlev, R. Y., A. S. Solomatin, N. B. Leonidov, I. I. Kulakova, G. V. Lisichkin, Detonation diamond—A perspective carrier for drug delivery systems, Russian Journal of General Chemistry, 84, 2014, 379-390.

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Tribological Journal BULTRIB Vol. 7, 2018
Papers from the 13th International Conference **BULTRIB '18**
25-27 October 2018, Sofia, Bulgaria
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TRIBOLOGICAL RESEARCHES OF TRIBOELEMENTS TOPOGRAPHY OF HOB MILLING PROCESS OF CYLINDRICAL GEAR SERRATION

(EXTENDED ABSTRACT)

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INTRODUCTION

Hob milling process is one of the most important links in the chain of machining because productivity, final geometrical accuracy and gear cutting are very dependent on it. The quality of the machining of gear serration is one of the conditions for achieving the required quality of the work-piece. In this paper the methodology for the identification of topography of tool teeth and gear serration produced by uncoated and coated model and real hob milling tool is presented. The research is realized mainly at the Faculty of Technical Sciences, University of Novi Sad and it is also based on cooperation between academic partners from Eastern and Central Europe.

GEAR CUTTING AND TOPOGRAPHY OF THE SURFACE

Hob milling, as one of the most complex machining processes, has the widest application in the process of gear cutting of cylindrical gears due to the high productivity of the process. The complicated kinematic and geometric relationships between the hob milling tool and the work-piece create a series of difficulties and problems that prevent the optimal use of tool and machine.

The hob milling tools with changeable teeth beside that they allow larger constructive back angles, they also have a relatively large, usable cutting length. Various variants of hob milling tools that combine different processes such as roughing and finishing and machining of chamfers for removing irregularities have also been developed.

Characteristic parameters formed during the technological process define macrogeometry and microgeometry of contact surfaces. The connection between topography of contact surfaces and the development of tribological processes is very complex. The change of topography in the development of tribological processes can be shown by the model as in the Fig. 1. For the correct analysis of tribological processes, but also tribologically correct construction, the roughness of the contact surfaces is especially significant.

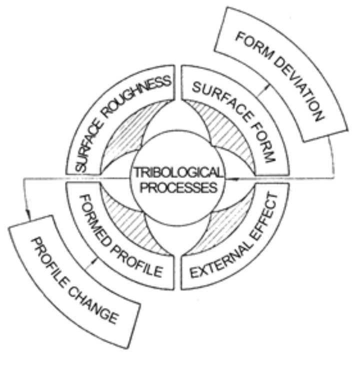

Fig. 1. Change of topography during development of tribological processes

It is known that for analysis of the roughness of the machined surface of the elements, there are more than 30 parameters that are less and those that are more represented. The basic parameters of roughness are defined according to national and international standards. The first three parameters Ra, Rmax and Rz represent a small group of the three most common parameters, while Rt, Rq and Rp are the parameters that are also used, but considerably less than the three previously mentioned roughness parameters.

RESEARCH OF TRIBOELEMENTS TOPOGRAPHY OF HOB MILLING PROCESS IN LABORATORY CONDITIONS OF GEAR CUTTING OF CYLINDRICAL GEARS

In the research of the process of hob milling of cylindrical gears serration long-term experimental tests are implemented by appropriate method and devices / integral hob milling tool, a device for model hob milling and a single-tooth tool /.

• Roughness parameters of lateral flank of model hob milling tools during gear cutting of cylindrical gears

This experimental study contains an analysis of the roughness parameters of the input and output side lateral flank of four subgroups of thirteen model hob milling tools. Some of the results for input lateral flank of uncoated tools are shown in figures below.

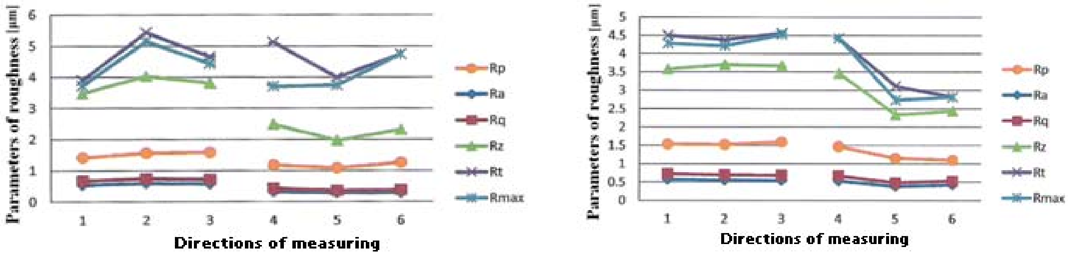

Fig. 2. Roughness parameters for unworn and worn-out tool with module m=3 mm

• Roughness parameters of the tooth-face of model hob milling tools

Part of the results for tooth-face of model tools are presented in next figure.

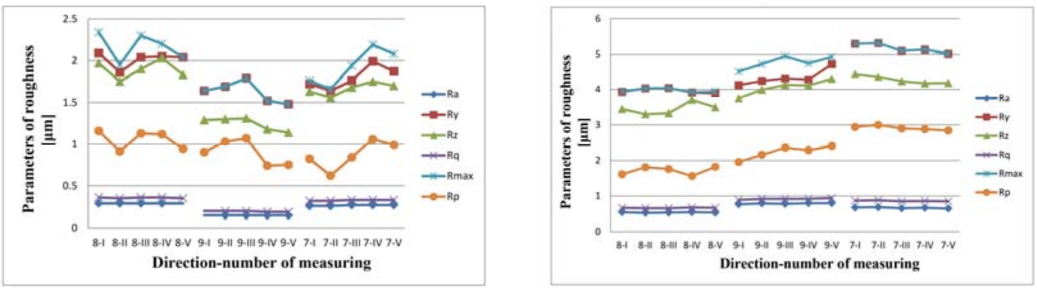

Fig. 3. Roughness parameters of coated and unworn tool with modules m=3 mm and m=5 mm

CONCLUSION

As can be seen from the results presented the roughness parameters Ra, Rq are parameters whose results are fairly uniform and their dissipation is insignificant. For the Rp roughness parameter, the dissipation is slightly higher than the parameters Ra and Rq, while the parameters of the roughness Ry, Rz, Rmax are the parameters in which the largest dissipation of the results is observed. The basic roughness parameters of the lateral flank and tooth-face of the model hob milling tools cannot fully define the quality of this surface, so it would be necessary to use stochastic indicators of roughness for a more complex and better quality assessment of the profile of the tribo-mechanical element.

ACKNOWLEDGMENTS

The research was funded by the ESTD Ministry of Serbia within the project III 43008, and it is the result of the cooperation within CEEPUS projects CIII-BG-0703-07-1819 and CIII-RS-0304-02-0910.

Tribological Journal BULTRIB Vol. 7, 2018
Papers from the 13th International Conference **BULTRIB '18**
25-27 October 2018, Sofia, Bulgaria
Society of Bulgarian Tribologists
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MODELING A BAR ELEMENT TO STUDY IMPACT PROCESSES IN ELASTIC-PLASTIC MECHANICAL SYSTEMS

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ABSTRACT

The paper is focused on modeling of a nonlinear bar element. The purpose is to study the elastic and plastic deformations of mechanical systems, caused by impact forces. The distribution of an impact wave in elastic-plastic mechanical system is considered based on a numerical example. In the current paper the influence of the period of action of the external force, the influence of the internal resistance and the influence of the mass distribution are defined. The problem is solved using Matlab Simulink.

***Keywords**: FEM, nonlinear bar element, plastic deformation*

Tribological Journal BULTRIB Vol. 7, 2018
Papers from the 13th International Conference **BULTRIB '18**
25-27 October 2018, Sofia, Bulgaria
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FRICTION INDUCED VIBRATIONS OF A CANTILEVER BEAM

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ABSTRACT

In the present work friction induced vibrations of a fixed support beam considered as a continuous system are studied. The dynamic model is made using FEM, as the internal damping is taken into account (Rayleigh damping). The friction force, applied on the beam is nonlinear function of the relative velocity of sliding and its modeled as a cubic function in its drop-down section. Stationary process of motion is considered in the study. The problem is solved using Matlab Slimulink. The numerical solution is confirmed by experiment.

Keywords: *Self-excited vibration, continuous system, FEM*

Tribological Journal BULTRIB Vol. 7, 2018
Papers from the 13th International Conference **BULTRIB '18**
25-27 October 2018, Sofia, Bulgaria
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INFLUENCE OF THE FRICTION GEO-MODIFIER ON THE ANTI-WEAR PROPERTIES OF PLASTIC LUBRICANTS

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ABSTRACT

The article describes the influence of the friction geo-modifier on the antiwear properties of greases and gear oils. Geo-modifiers of friction are the fine powders of mineral materials. The work is directed on the investigation the influence of the geo-modifiers of friction in the form of the hard lubricant compositions, which based on a mineral serpentinite, on the anti-wear properties of plastic lubricants. This composition is the fine powder serpentinite with the addition of components such as chalk, borax, kaolin and talc. We compared the antiwear properties of the greases without geo-modifiers of friction and the antiwear properties of greases containing the geo-modifiers of friction from 1% to 3%. The Litol-24, Shell Gadus S3, Mobilgrease XHP 222, Castrol LMX was used for testing. The four-ball machine of friction was used for tests. As geo-modifiers the serpentinite was used, the fraction of which has a size from 0.87 microns to 2.2 microns. The parameter “wear scar diameter” was used for evaluation of the antiwear properties of lubricants.

This work was supported by the Ministry of Education and Science of the Russian Federation (grant No 9.7881.2017/8.9).

Keywords: *geo-modifier of friction, serpentine, plastic lubricant, wear scar diameter*

Tribological Journal BULTRIB Vol. 7, 2018
Papers from the 13th International Conference **BULTRIB '18**
25-27 October 2018, Sofia, Bulgaria
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DYNAMICAL STRESSES IN THE HIGH CLASS WIND TURBINE BLADES CAUSED BY THE VERTICAL WIND SPEED GRADIENT. PART 1 - AERODYNAMICAL LOADS

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ABSTRACT

For the powerful wind turbines having large dimensions, the aerodynamic interaction becomes a function of the angle of the turbine rotation (azimuth angle), dues to the impact of the vertical gradient of the wind speed. This distribution is in result of a multitude of a tribological and thermodynamics factors. The authors of this study in previous researches show that this results in significant dynamic loads on the turbine blades. Furthermore, the longitudinal turbulence of the wind speed introduces additional dynamic excitation. The investigation of these dynamic loads is the main objective of this study.

***Keywords**: wind turbine, vertical distribution and longitudinal turbulence of wind, aero-dynamic loads*

Tribological Journal BULTRIB Vol. 7, 2018
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DYNAMICAL STRESSES IN THE HIGH CLASS WIND TURBINE BLADES CAUSED BY THE VERTICAL WIND SPEED GRADIENT. PART 2 - STRESS ANALYSIS IN THE TURBINE BLADES

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ABSTRACT

In the first part of the study, are obtained the distributions of the thrust and torque forces along the turbine blades of the high class wind turbines, as variable functions of the time, derived as a complex result of accounting the vertical gradient and the longitudinal turbulence of the wind speed. On the base of this, this second part perform a stresses analysis of the turbine blades. The turbine's blades are considered as Euler-Bernoulli beam under the impact of the trust and torque forces as well as of the centrifugal forces. The Finite elements method is applied in for the solving of the partial differential equations describing the model under consideration. It is using two nodes for an element, with of four degrees of freedom for each nodes and a cubic polynomial approximation of the modal shapes. The deformations are relatively small within the separated finite elements and this gives possibility for applying the superposition principle.

***Keywords**: wind turbine, vertical distribution and longitudinal turbulence of wind, dynamic loads, Finite elements method.*

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OPTIMIZATION OF MEMS PIEZOELECTRIC ENERGY HARVESTERS WITH INTERDIGITATED ELECTRODES

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ABSTRACT

A method for optimization of piezoelectric voltage of vibrating MEMS energy harvester with respect to the output voltage is considered in the paper. The investigated vibrating elements are cantilevers and doubly clamped beams with piezoelectric thin film layers. Interdigitated electrodes are applied at the top surface of piezoelectric layers in order to increase the efficiency of the energy harvester. The non-uniform distribution of piezoelectric charges along vibrating structure is a result of non-uniform distribution of bending stress. The length and position of the piezoelectric layers on the elastic surface have to be chosen in such way so to avoid the electric charges decrease or total output energy termination. The aim of optimization method described in the paper is to determine the optimal length and position of the piezoelectric interdigitated electrodes on the surface of the elastic beam in such way so the maximum output voltage to be obtained with minimal lengths of the piezoelectric layers.

Keywords: Energy harvester, MEMS, vibration, interdigitated electrodes, cantilever, doubly clamed beam

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25-27 October 2018, Sofia, Bulgaria
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ACOUSTIC METHOD FOR IDENTIFICATION OF RAILWAY WHEEL DISC STRUCTURAL VIBRATIONS USING COMSOL

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ABSTRACT

An investigation of structural vibrations of a simplified disc model of a railway wheel is treated in this study. A numerical investigation of the structural vibrations of a finite element model of the disc is investigated using COMSOL software. An experimental setup is built and used to verify the numerical results. The excitation is caused by the impact hammer and the sound pressure is measured to obtain vibrations response. Based on the results, a method for identification of the disc structural vibrations and noise radiation is verified and few useful conclusions have been made. These results could be used in the process of future investigation and design of low-noise railway wheels.

Keywords*: railway wheel, structural vibrations, sound pressure level.*

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Papers from the 13th International Conference **BULTRIB '18**
25-27 October 2018, Sofia, Bulgaria
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TRIBOLOGICAL CHARACTERISTICS OF AUSTEMPERED DUCTILE IRONS WITH NANOSIZED PARTICLES

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ABSTRACT

The samples of austempered ductile irons (ADI) with nanosized particles of TiCN+TiN, TiN and cBN are investigated. The austempering mode consists of heating at 900°C, 1 h and isothermal retention at 380°C, 2 h. The obtained structure of the upper bainite is examined by an optical metallographic microscope GX41 OLIMPUS. SEM and EDX analyses of cast samples with nanosized particles are performed. Wear test is carried out of ADI samples on thumb-disc circuit during friction on the fixed abrasive. The influence of nanoadditives on the tribological characteristics, hardness and microstructure of ADI is established.

Keywords: *nanosized particles, austempered ductile irons, upper bainite, wear resistance, hardness*

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DEVICE AND METHOD FOR SIMULTANEOUS DETERMINATION OF ROLLING AND SPINNING FRICTION IN A CONCENTRATED CONTACT

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ABSTRACT

This paper presents the methodology and its related device for the simultaneous determination of the spinning friction moment and the rolling friction moment in a concentrated contact.
The method is illustrated by a concrete example, the values obtained for the two coefficients being in the order of the microns in accordance with other papers and with the roughness characteristics of the ball and rod surfaces.

Keywords: *spinning friction, rolling friction, experimental*

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GENERAL METHODOLOGY FOR STUDYING THE TRIBOLOGICAL PROCESSES ON THE BASIS OF THE COMMUNICATIVE POTENTIAL

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ABSTRACT:

The paper presents the authors general procedure for tribological processes study based on the communication potential and the general law of contact interaction in tribology. The procedure is applicable for arbitrary scope of perturbation influence, if the scope is divided in sectors where the communication potential varies in a monotone.

The procedure was implemented for a concrete case of static friction study in a contact system containing high-strength cast iron with various tin micro-alloys. The obtained results are as follows:

- Procedure is developed and experimental relationship is obtained for the static coefficient of friction variation with the content of tin.
- The communication potential of the static friction is attained and its experimental variation is obtained for the content of tin in the interval 0% to 0,032% .
- The law for variation of the total communication potential with the content of tin in the interval 0% to 0,032% is obtained .
- The law for the static coefficient of friction variation with with the content of tin in the interval 0% to 0,032% is obtained.

The results obtained are not duplicated in the literature and are not published by the authors.

This study and the results are related to the implementation on tasks:

(a) Contract: ДН 07/28-15.12.2016 “Research and creation of new wear-resistant coatings using composites and nanomaterials”, funded by the National Science Fund at the Ministry of Education and Science, Bulgaria;

(b) CEEPUS III Network: CIII-BG-0703-07-1819 “Modern Trends in Education and Research on Mechanical Systems – Bridging Reliability, Quality and Tribology”.

(c) Project FSI-S-17-4415 from the Ministry of Education, Youth and Sports of Czech Republic.

Keywords*: tribology, contact interaction, relationships and laws, friction, high-strength cast iron*

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WEAR OF GAS-FLAME COMPOSITE COATINGS WITH TUNGSTEN AND NICKEL MATRIX. PART I. ABRASIVE WEAR

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ABSTRACT

The paper presents the authors general procedure for tribological processes study based on the communication potential and the general law of contact interaction in tribology. The procedure is applicable for arbitrary scope of perturbation influence, if the scope is divided in sectors where the communication potential varies in a monotone.

The procedure was implemented for a concrete case of static friction study in a contact system containing high-strength cast iron with various tin micro-alloys. The obtained results are as follows:

- Procedure is developed and experimental relationship is obtained for the static coefficient of friction variation with the content of tin.
- The communication potential of the static friction is attained and its experimental variation is obtained for the content of tin in the interval 0% to 0,032% .
- The law for variation of the total communication potential with the content of tin in the interval 0% to 0,032% is obtained .
- The law for the static coefficient of friction variation with with the content of tin in the interval 0% to 0,032% is obtained.

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(c) Project FSI-S-17-4415 from the Ministry of Education, Youth and Sports of Czech Republic.

Keywords: *HVOF coatings, tribology, abrasion wear, erosion wear*

Tribological Journal BULTRIB Vol. 7, 2018
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WEAR OF GAS-FLAME COMPOSITE COATINGS WITH TUNGSTEN AND NICKEL MATRIX. PART II. EROSIVE WEAR

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ABSTRACT

Object of investigation are the characteristics of wear and wear resistance of composite powder coatings, deposited by supersonic flame stream (High Velocity Oxygen-Fuel HVOF spraying). Two groups of coatings have been obtained – powder composites of tungsten and nickel matrices, where each group includes coatings of different size of powder particles. The coatings are tested in two cases - during abrasion and erosion. The research work consists of two parts. The first part represents results on wear characteristics during dry friction on the surface with fixed abrasive particles. The present publication represents the second part of the study. Results are given here on the wearing of coatings under the effect of air stream, carrying solid abrasive particles /erosion wear/, particularly – mass erosion wear, erosion rate, erosion intensity, absolute and relative wear resistance under identical conditions of erosion. It has been found out that upon increasing the size of the particles 4 times from 11 to 45 microns in the case of coatings with tungsten matrix the wear resistance grows up 2.1 times, while in the case of coatings with nickel matrix the growth of the erosion resistance is insignificant – 1.2 times. Comparative results on wear of the tested coatings during abrasion and erosion show different tendencies in the influence of the size on wear and on wear resistance. The abrasive wear resistance of both kinds of coatings is greater in the case of smaller sizes of powder particles. The same coatings in case of erosion are of lower wear resistance, i.e. lower resistant ability under impact effect of the abrasive particles in air stream.
The obtained results have not been reported so far in the current literature and they have not been published yet by the authors.

This study and the results are related to the implementation of the tasks:
(a) Contract: ДН 07/28-15.12.2016 "Research and creation of new wear-resistant coatings using composites and nanomaterials", funded by the National Science Fund at the Ministry of Education and Science, Bulgaria;
(b) CEEPUS III Network: CIII-BG-0703-07-1819 "Modern Trends in Education and Research on Mechanical Systems – Bridging Reliability, Quality and Tribology";
(c) Project FSI-S-17-4415 from the Ministry of Education, Youth and Sports of Czech Republic

Keywords: *HVOF coatings, tribology, abrasion wear, erosive wear*

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INFLUENCE OF ADDITIVES ON STRUCTURAL AND PHYSICO-MECHANICAL PROPERTIES OF NANO-MICROCRYSTAL ALUMINIUM ALLOYS

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ABSTRACT

Al-Fe-V-Si alloys are promising materials for the space and automotive industries. The ribbons are obtained by a plurality of planer flow casting technique. The purpose of this work is to analyze the influence of additional particles on the microstructure of aluminium ribbons. Two types of microstructure are observed. Microhardness (Vickers) is measured with a hardness tester and a NanoScan microscope.

Keywords: *Nano-microcrystalline Al-Si alloys, nanostructure, microhardness*

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25-27 October 2018, Sofia, Bulgaria
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FIT – Technical University of Sofia

DIRECT METAL DEPOSITION FOR HYBRID MANUFACTURING

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ABSTRACT

The presented paper concerns the controllable parameters for direct metal deposition technology (DMD). It demonstrates milestone stages of the part production using direct metal deposition and achieved accuracy. A complex part - turbine blade was used as an example. The obtained results have no analogue in the current literature and they have not been published by the authors.

This study and the results are related to the implementation on the task:
Project D-063-2018/20.06.2018 “Research of capabilities of additive technologies for building metal structures with direct and indirect methods”.

Keywords: *Direct Metal Deposition, Rapid Prototyping, Additive Technology, Turbine Blade*

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Papers from the 13th International Conference **BULTRIB '18**
25-27 October 2018, Sofia, Bulgaria
Society of Bulgarian Tribologists
FIT – Technical University of Sofia

VIRTUAL PROTOTYPE OF FAMILY BASED GRAPPLE DESIGN

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ABSTRACT

This article provides a virtual based functional analysis and friction reduction of a grapple and a concept for grouping the different grapple parts in modules with the main purpose to show the ability of designing grapple families in which the different size grapple is formed by existing logical modules. Using the modular approach for designing families further provides easier and faster optimized manufacturing and logistics, lower cost price, shorter delivery times and met customers' requirements.

Keywords: *virtual prototyping, concept design, optimization, modular design, grapples*

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Papers from the 13th International Conference **BULTRIB '18**
25-27 October 2018, Sofia, Bulgaria
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SCIENTIFIC LITERATURE ON THERMAL SPRAY COATINGS FROM SOUTHEASTERN EUROPE: A TEN YEARS BIBLIOMETRIC ANALYSIS

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ABSTRACT

In recent years there is an increasing number of articles presenting and/or analysing the scientific production from discrete geographical regions on a certain scientific topic. These articles applied the so-called bibliometric methods in order to evaluate the contribution of different countries in a scientific research field. In the present work, the research output of all countries in Southeastern Europe (SEE) on the scientific topic of thermal spray coatings is presented by using bibliometric indices such as the total number of publications and citations as well as the *h*-index and the average number of citations per publication. Analysis spans the last ten years and the required scientific data in order to calculate the bibliometric indices were retrieved using the Scopus® scientific database.

The obtained results are not duplicated in the literature and have not been published yet by the authors.

This study and the results are related to the implementation on the tasks:

(a) Projects TR 34028 and TR 35021, supported by the Republic of Serbia, Ministry of Education, Science and Technological Development;

(b) Contract: ДН 07/28-15.12.2016 “Research and creation of new wear-resistant coatings using composites and nanomaterials”, funded by the National Science Fund at the Ministry of Education and Science, Bulgaria;

(c) CEEPUS III Network: CIII-BG-0703-07-1819 “Modern Trends in Education and Research on Mechanical Systems – Bridging Reliability, Quality and Tribology”.

***Keywords**: thermal spray coatings, Southeastern Europe, bibliometric indices, scientific publications, Scopus database*

Tribological Journal BULTRIB Vol. 7, 2018
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ELECTROLESS NICKEL COATING OF CARBON MICRO FIBERS AND NANOTUBES INTENDED FOR A REINFORCING PHASE IN MMC AND PMC

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ABSTRACT

The paper concerns the study of electroless nickel coating of carbon microfibers (CFs) and carbon nanotubes (CNTs) in order to be utilised as reinforcing phase for composites with metal and polymer matrix. The efficiency of the developed alkaline solution based on two salts – nickel sulphate ($NiSO_4$) and nickel chloride ($NiCl_2$) for nickel alloy coating (Ni- P) onto the CFs and CNTs was confirmed. The electroless Ni-P coating of CNTs was performed at room temperature under conditions of ultrasonic bath treatment, which assist avoiding excessive agglomeration during metallization.

Keywords: *Carbon fibres, Carbon nanotubes, Electroless nickel coating, MMC, PMC*

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25-27 October 2018, Sofia, Bulgaria
Society of Bulgarian Tribologists
FIT – Technical University of Sofia

CHARACTERIZATION ON ZrN COATINGS DEPOSITED BY DC MAGNETRON SPUTTERING

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ABSTRACT

The ZrN coatings were deposited on 304L and R18 steel substrates by means DC magnetron sputtering method. The structure of the coating was observed by X-ray diffraction. The hardness and elastic modulus was measured. The wear resistance of the coatings was investigated. ZrN films has a face-centered cubic structure; nanohardness is H=31.273±5.8 GPa and elastic modulus - E=291.469±39.809 GPa for ZrN on 304L substrate; H=19.016±2.151 GPa and E=219.147±169.918 GPa for ZrN on R18 steel.

Keywords: *Magnetron sputtering, ZrN coatings, hardness, elastic modulus, wear resistance*

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Papers from the 13th International Conference **BULTRIB '18**
25-27 October 2018, Sofia, Bulgaria
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ABRASIVE WEAR OF ULTRA-HIGH-MOLECULAR-WEIGHT POLYETHYLENE, MODIFIED WITH CARBON NANOTUBES

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ABSTRACT

The present study presents comparative results on the wear and wear-resistance characteristics of Ultra-High-Molecular-Weight Polyethylene (UHMWPE) samples containing a different concentration of carbon nanotube (CNTs) additive: 0.5%, 0.75%, 1% and 1.5% at dry abrasive friction and abrasive friction when lubricated with sea water. The test samples are made from UHMWPE with the addition of carbon nanotubes with nickel coating and carbon nanotubes without nickel coating.
Results of mass wear, velocity, wear intensity, absolute and relative wear-resistance of samples with carbon nanotubes with and without nickel coating were obtained. The highest abrasion resistance was found to have UHMWPE samples containing 1% carbon nanotubes without nickel coating.

***Keywords**: abrasive wear, UHMWPE, carbon nanotubes, composite materials*

Tribological Journal BULTRIB Vol. 7, 2018
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IMPROVING THE TRIBOLOGICAL CHARACTERISTICS OF HELICAL DRILLS FROM HIGH SPEED STEEL BY MEANS OF A CONTACTLESS LOCAL ELECTRICAL DEPOSITION WITH COMPOSITE CARBIDE ELECTRODES BASED ON TiC AND TiN

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ABSTRACT

In this work was conducted a study of the wear of drills from high-speed steel HS-5-2 at cutting of carbon steel 45(with 0, 45%C). The tools are coated with new non-tungsten carbide composite materials based on TiC, TiN and TiCN. The coatings are applied by contactless Local Electro Spark Deposition - LESD. The complex influence of the electrical parameters of the deposition process and the electrode materials, (respectively the morphology and composition of the coatings) onto the wear of the drills, and on the contact processes during cutting were investigated. It has been found the nature of the amendment of the wear depending of the layering electrode materials and of the parameters of the LESD mode. The use of the new non-tungsten electrodes results in an increase in the durability of the coated drills more to 1.9÷2.5 times as compared than the non-coated ones and up to 1.4 times than that of the coated with electrodes based of tungsten carbide. The technological conditions in which are obtained a minimal wear of the layered drills are determined. The wear analysis show that the LESD can successfully be used for increasing wear resistance of drills, but in order to obtain maximum a durable and reliable tribological effectiveness is needed preliminary optimization of parameters of the regime and materials for deposition according to the specific cutting conditions.

Keywords: *coatings, electrode materials, non-tungsten carbides, wear, roughness, microhardness, phase composition*

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Papers from the 13th International Conference **BULTRIB '18**
25-27 October 2018, Sofia, Bulgaria
Society of Bulgarian Tribologists
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COMPARATIVE STUDIES OF TRIBOLOGICAL CHARACTERISTICS OF CARBON STEELS WITH GAS FLAME COATINGS FROM NEW MULTI-COMPONENT CARBIDE COMPOSITE MATERIALS

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ABSTRACT

A new type of wear-resistant and high-hard composite coatings with a complex structure and different phase composition has been obtained and studied in the present work by gas-fuel spraying on carbon steels. The choice of powder compositions is made in order to maximise the adhesion and wear resistance of the resulting coatings, and hence the operating lifetime of the contact surfaces in terms of resistance to abrasion. For this purpose, are selected conventional composite powders - semi-self-fluxing alloys based on Ni-Cr-Co-B-Si to which tungsten carbide alloys BK8 have been added, and ultra-hard phases - WC, TiB_2, B_4C and others both individually and in combinations with each other in different ratios. The wear of the coatings under conditions of dry friction is investigated. It has been found that new composite coatings have repeatedly reduced the wear of the coated surfaces. The influence of the B_4C, TiB_2 and WC on the rate of wear and on wear resistance, as well as the relation of abrasive wear with the proportions of components in the powder compositions, has been determined. On the basis of the experimental data and comparative analysis, appropriate materials for deposition of coatings with optimum tribological properties have been defined.

Keywords: *Gas flame spraying, WC, B_4C, TiB_2, wear resistance coatings, microstructure, microhardness, self-fluxing alloys*

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MATHEMATICAL MODEL FOR THE ANALYSIS OF OPERATING CONDITIONS OF HYDRODYNAMIC TRIBO-SYSTEMS AND FRICTION PROCESSES AND WEAR OF THEIR CONTACT SURFACES

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ABSTRACT

This article describes, develops and applies approach of the interaction of rough surfaces for one of the tasks of simulation of tribological systems of the piston engine. In this paper we described the general approach to building a model of interaction between rough surfaces, leading to the analysis of the Markov process. Given the initial data and the method of calculating the trajectory of movable elements on the lubricating layer, we determined the tribological parameters defining the service life of tribological systems of the piston engine on the example of crankshaft bearings.

Keywords*: surface asperities interaction, Markov process, tribological parameters, crankshaft bearings*

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BEM THEORY ADAPTATION TAKING INTO ACCOUNT NON-UNIFORM, NON-STATIONARY WIND FIELD

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ABSTRACT

The powerful wind generators, producing electric power on the order of megawatts are with significant sizes. The studies on the interaction between the airflow and the wind turbine usually assume that the airflow is homogeneous in vertical direction, which admission is made also in the classical Blade element momentum (BEM) theory. For the powerful generators the vertical gradient of the wind velocity causes a dependence of the aerodynamic interaction from the azimuth angle and leads to a significant cyclic variability of the forces and moments acting on the blades.

Keywords: *BEM theory, vertical speed gradient, wind generators*

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MODIFIED BEM THEORY APPLICATION FOR DETERMINING THE AERODYNAMIC FORCES ACTING ON THE BLADE OF WIND TURBINE

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ABSTRACT

The wind generators generating power in the order of megawatts have significant dimensions. Due to the vertical wind speed gradient in these plants it is important to note that the aerodynamic interaction is a function not only from the wind speed at the level of the turbine axis bat also from the blade's azimuth position. The authors propose the adaptation of the BEM theory to take into account the different aerodynamic conditions for the separated blades at a given angle of the turbine rotation. In this article are given more detailed the obtained results for the aerodynamic characteristics and forces in compared to the classical approach.

Keywords: *power wind turbine, vertical speed gradient, aerodynamic forces*

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DYNAMIC STRESS ANALYSIS OF A BLADE OF WIND TURBINE GENERATOR TAKING INTO ACCOUNT VERTICAL WIND SPEED GRADIENT

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ABSTRACT

For the large megawatts wind turbines the authors has been investigate that due to the vertical wind speed distribution arise dynamical variable loads of the turbine blades that are functions of the azimuth angle. In an addition the longitudinal turbulence of the wind speed introduces additional dynamic excitation. The investigation of the stress caused by these dynamic loads on the turbine blades in the upwind direction is the main publication task. The blades are considering as an Euler-Bernoulli beam. Finite element method is applied in for the solving of the obtained model.

Keywords: *dynamic analysis, continuous system, harmonic response, finite element method*

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METAL-METAL COMPOSITES WITH ZN-AL ALLOY BASE AND ADDITION OF TI MICROPARTICLES REINFORCED WITH CERAMIC NANOPARTICLES

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ABSTRACT

The zinc-aluminium casting alloy ZA-27 is well-established alloy and is frequently used material for plain bearing sleeves. It has good physical, mechanical and tribological properties. Its tribological properties can be further improved by adding hard ceramic microparticles to the alloy, i.e. by producing the metal matrix composites. However, the addition of ceramic particles usually decreases the ductility of the alloy. To overcome this, ceramic microparticles in the composites are replaced by 1 or 2 wt. % titanium microparticles (particle size approx. 10 μm). Titanium is quite ductile and has relatively low density and high strength. It is recognized for its high strength-to-weight ratio. Titanium melting point is much higher than the matrix alloy, and it is assumed to have an effect on improving the mechanical properties of the composite at elevated temperatures. Small amount (0.5 wt. %) of ceramic nanoparticles (particle size 20 – 30 nm) are also used, with the aim to increase the composite mechanical and tribological properties through some of the strengthening mechanisms, without lowering ductility of the composite. Structure of the composites was examined and their basic mechanical and tribological properties were tested. The results are evaluated and compared with the matrix alloy.

Keywords: *ZA-27 alloy, metal-metal composites, nanoparticles, microstructure, friction, wear*

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SELF-ORGANIZATION OF FRICTION CONDITIONS WHEN USING REPAIR AND RECOVERY ADDITIVES TO LUBRICANTS

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ABSTRACT

The studies of self-organization, energy dissipation, abnormally weak friction, the effect of Rebinder and "no-wear effect" in machine and technical joints, which are corner stones of synergetics, allowed to formulate the concept of "engines' maintenance and repair without disassembling and while running".

The results of tribological tests of the metalorganic additive «Renom Engine» indicated its high efficiency for use as a repairing tool for recovery of motor and tractor engines functionality.

It should be noted that the process of formation of a stable servovite is quite long, and most importantly, gradual process. Thus, there is no immediate improve of technical characteristics of the treated machine, but there is always a positive dynamics.

Based on exploitation tests it was found that the use of the metalorganic additive «Renom Engine» enables to restore the engine compression, to reduce the carbon monoxide concentration in the exhaust gases three times, to save up to 10% of lubricant and fuel, as well as to provide an easier start-up and stable operation of the engine.

The paper presents results of laboratorial tribological and operational tests of various metalorganic additives (repairing and maintenance compositions) including those created by nanotechnology, and introduces a concept of engines' maintenance and repair without disassembling.

Keywords: *self-organization, repairing and maintenance products, tribological tests of metalorganic additives, nanotechnology*.

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A GREAT TECHNICAL TAMPING WHICH WAS CONSIDERED A PROMOTING DISCOVERY. MICRO-TEXTURING OF THE SURFACE OF THE PROSTHETIC FEMORAL HEAD TO REDUCE FRICTION AND WEAR

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ABSTRACT

The paper refers to a technical solution that has raised much interest and has been published in a relatively large number of works, even in prestigious journals. This is the micro-texturing of the femoral head surface. It examines the validity of the possibility of increasing the durability of the hip joint, as a result of the improvement of its lubrication by micro-texturing of the femoral head surface. The paper focuses on the micro-texturing of the Co-Cr femoral head surface using a scheduled multi-indent technique. Although experimental studies have shown that the micro-texture solution cannot be applied to hip prostheses, there is still a gain: the use of the multi-indentation technique used to achieve micro-texture of surfaces for other industrial uses.

Keywords: *total hip prosthesis*, micro-texturing, multi-indentation, Co-Cr alloy, friction

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THE TRUNION FRETTING AND WEAR OF THE STEM OF TOTAL HIP PROSTHESIS AND ITS INFLUENCE ON THE PROSTHESIS STABILITY

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ABSTRACT

This work refers to the fretting phenomenon and the fretting wear manifested at the conical trunion between the stem and the femoral head of the classic hip prosthesis, metal - UHMWPE, as additional factor influencing the loss of the stability of the prosthesis over time. This wear cannot be monitored during the in vivo functioning of the prosthesis, but it is obvious by analyzing the hip prosthesis replaced after surgical intervention. Unfortunately, wear debris could not be highlighted, but only the wear scars produced on the conical trunion of the femoral stem.

Keywords: *hip prosthesis stability, conical junction, fretting wear, mechanical loading*

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ABOUT ENERGY BALANCE OF FRICTION AND MACHINE AS TRIBOSUPERSYSTEM

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ABSTRACT

Machine is regarded as tribosupersystem, which is composed of subsystems – tribosystems. From the position of energy-entropy analysis of adaptive-dissipative nature of states and properties of tribosystem a generalized machine rule is suggested. An idea is discussed about natural and real tribosystems and machines. A set of fundamental principles of tribosynthesis in natural and real machines is singled out.

Keywords: *machine, tribosystem, energy, enthropy, balance, reliability, damageability, wear, tribosynthesis*

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NON-TOXIC ANTIWEAR ADDITIVE FOR FOOD AND BIODEGRADABLE LUBRICANTS

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ABSTRACT

The possibility of using esters of citric and aconitic acids as antiwear (AW) and extreme pressure (EP) additives to vegetable oils has been investigated. The aim of the study is to develop completely non-toxic AW / EP additives for a number of lubricants. Such materials include both biodegradable lubricants based on vegetable oils and lubricants based on synthetic hydrocarbons for food processing equipment. It has been established that esters of polybasic acids and aliphatic alcohols can exhibit antiwear properties at a level comparable to zinc dialkyldithiophosphates. The possibility of increasing the solubility of such additives in vegetable oils at low temperatures when using a mixture of different alcohols for the esterification has also been clarified.

Keywords: *citric acid esters, aconitic esters, biodegradable lubricants, food equipment lubricants, non-toxic AW/EP additives*

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PREDICTING LIFETIME OF INTERNAL COMBASTION ENGINE CRANKSHAFT JOURNAL BEARINGS AT THE DESIGN STAGE

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ABSTRACT

The purpose of the article is to predict the service life of the connecting rod bearing of an internal combustion engine. The technique of calculation is based on lubrication hydrodynamic theory and the molecular-mechanical theory of friction and wear fatigue theory. It includes several stages.The first is to set the load conditions of the engine. The second is the definition of the forces acting on the connecting rod bearing. The third is the calculation of the hydromechanical characteristics of the bearing such as the minimum thickness of the lubricating layer, the maximum hydrodynamic pressure, the loss of power for friction, and others. The fourth is the definition of the duration of the zone where liquid friction is violated. The fifth is the calculation of bearing wear for 720 degrees of crankshaft rotation (loading cycle) for each mode. Then the wear is recalculated taking into account the duration of each mode of operation. The characteristics of the crank journal and bearing are taken into account. The diagram of the wear of the connecting rod bearing is based on the simulation results. This work has been carried out within financial support of Russian Foundation for Basic Research (project № 16-08-01020\16).

Keywords: *service life, connecting rod bearing, wear*

Tribological Journal BULTRIB Vol. 7, 2018
Papers from the 13th International Conference **BULTRIB '18**
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INVESTIGATION OF THE EFFECT OF NON-ISOTHERMAL FLOW OF NON-NEWTONIAN FLUID IN A THIN LAYER AND THERMAL STATE OF THE TURBOCHARGER RADIAL BEARINGS ON THE ROTOR DYNAMICS

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ABSTRACT

The most of the theoretical and experimental works on the study of friction units are based on the classical hydrodynamic theory of lubrication. In the presented study, a system of equations for hydrodynamic problems that take into account the processes of heat exchange between a lubricant and a solid is given. To model non-Newtonian properties of modern lubricants, a rheological model of the lubricant was used. A series of comparative calculations for evaluating the performance of hydrodynamic units, taking into account their thermal loading, is performed on the example of calculating the dynamics of a flexible asymmetric rotor. The results of the calculations showed that the temperature difference between the rotor bearings was 15-18 degrees. The results of theoretical studies have shown good agreement with the results of experimental studies.

This work was carried out with the financial support of the Russian Foundation for Basic Research (Project No 16-08-01020 / 16) and the Ural Branch of the Russian Academy of Sciences (Project No 0407-2015-0005).

Keywords: *non-Newtonian fluid, thermal state, bearing, rotor*