THEORETICAL AND EXPERIMENTAL RESEARCHES CONCERNING THE ADHESION OF THE SUPERFICIAL LAYERS OBTAINED FROM AMORPHOUS ALLOYS BY THERMAL SPRAYING WITH PLASMA JET

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Abstract: *The deposit by the thermal spraying with plasma jet is a technological procedure with material contribution to which the layer grows up by the incremental depositing of the particles thermal sprayed on the sub-layer, so the increasing of the layer's thickness is rapid, but the process itself is stochastic.*

For the adhesion of the layer thermal sprayed to the basic sub-layer, the particles, for a good flattening, must have the following conditions: an impact speed (v_p) higher than a critical speed (v_{cr}) and the particle temperature (T_p) must be higher than a critical melting temperature (T_{cr}). The particle in fluid state to the impact with the sub-layer is flattening, thus realizing a particle – basic sub-layer – environment heat exchange until its complete solidification.

The depositing of such layers is made in order to recondition some used spare parts or to increase their resistance to wear.

Keywords: *deposit, thermal spraying, adhesion, resistance to wear*

1. INTRODUCTION

In most cases, the parts of different engines, machines, equipments etc. are out of order by the damage of the contact surfaces (concerted), due in general to the wear processes of different types (adhesive, abrasive wear, superficial, tribo – chemical tiredness etc.) or / and to some chemical corrosion processes. In these conditions, the respective parts when reach a certain degree of damage are replaced (the changeable parts) or are reconditioned by various proceedings (build – up welding, thermal spraying, electrical, chemical and electrolytic, plating etc.) if this is justified from the technical and economic point of view [3].

In some cases there are made preventive coverings by the depositing of some superficial layers that may increase the resistance to wear and / or corrosion. The problem of obtaining superficial layers is complex and in the figure 1 there is presented diagrammatic the system superficial layer – sub-layer with four distinct zones.
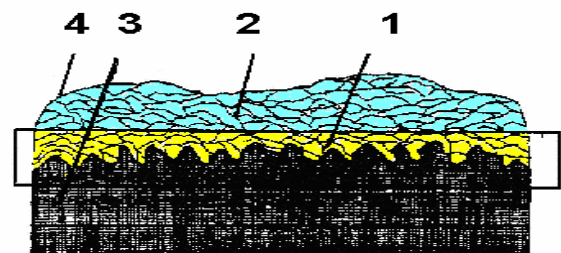
Figure 1. The complex system: layer – sub-layer [4].

The components and the properties of these four zones are: 1- the interface (adhesion, inter-diffusion, the layer – sub-layer physical and chemical interaction); 2 – the superficial layer (cohesion, superficial tension, mechanic properties, micro-structure); 3 - the sub-layer or the basic material (mechanic properties, thermal properties); 4 – the contact surface with the concerted part or with the environment (roughness, resistance to wear and corrosion, porosity).

2. THE ENERGETIC BALANCE SHEET OF THE PARTICLE TO THE IMPACT WITH THE SUB-LAYER

For the adhesion of the layer thermal sprayed to the sub-layer / basic layer, for a good flattening, the particles must have the following conditions: an impact speed v_p higher than a critical speed v_{cr} and the particle temperature T_p higher than a critical / melting temperature T_{cr}.

The particle in fluid state, having the speed v_p şi temperature T_p, to the impact with the sub-layer la is flattening (the particle's flow on the sub-layer) realizing a heat change particle – sub-layer – environment till the particle's complete solidification as it may be seen in the figure 1[3]. To the particle's impact with the melted material with the sub-layer it happens an energy change between the parts and the energetic balance sheet to the particle – sub-layer interaction is given by the equation:

$$E_t = E_v + E_s + E_i + E_{ti} + E_m + Q_c \ , \ [J] \quad (1)$$

where: E_t represents the particle total energy between the impact and it is given by the relation (2):

$$E_t = m_p \cdot \frac{v_p^2}{2} + m_p c_l (T_s - T_N) + m_p L_t + m_p c_s (T_t - T_{ss}), [J] \quad (2)$$

where: m_p is the particle mass, in [kg];

c_l – the specific heat of the particle in liquid state, in [J/kg·K];

c_s - the specific heat of the particle in solid state [J/kg·K];

T_s – the overheat temperature (T_t - the melting particle temperature), in [K];

T_N – the temperature of the alloy homogeneity nucleus, in [K];

L_t – latent solidification heat, in [J/kg];

T_{ss} – sub-layer heat, in [K].

E_v - distortion viscous energy necessary to the particle flattening given by the relation (3):

$$E_v = \int_0^{\tau_f} \int_v \eta \cdot \left[\left(\frac{\partial v_r}{\partial y} \right)^2 + \left(\frac{\partial v_z}{\partial r} \right)^2 \right] \cdot dv \cdot d\tau, [J] \quad (3)$$

where: η is the dynamic viscosity of the particle, in [Pa·s];

τ – the flattening particle time in [s];

v_r , v_z – the distortion speed components in cylindrical coordinates after the directions r respectively z [6], in [m/s];

E_s – the superficial energy that derives from the shape change meaning the passing from the spherical shape to the flattened particle, in [J];

E_i – the inter-phasic reaction energy that is named also the cohesion – adhesion energy, in [J];

E_{ti} – the energy gathered in the flattened particle under the form of residual internal tensions, in [J];

E_m – the energy gathered in the flattened particle to crystallization or to the passing in amorphous state, in [J];

Q_c – the heat yielded by the particle to the environment and to the sub-layer, in [J];.

The energies E_v, E_s, Q_c are consumed to the viscous distortion, the shape (flattening) change of the particle after the impact and to the heat yielding and the energies E_i, E_{ti} and E_m stay in the particle under different shapes. In the case of rapid cooling the latent crystallization heat is no longer relieved ($L_t = 0$, $T_N = 0$) and the equation (2) becomes:

$$E_t = m_p \frac{v_p^2}{2} + m_p c_{ls} (T_s - T_{ss}), [J] \quad (4)$$

where: c_{ls} is the average specific heat of the overcooled liquid and of the amorphous solid, in [J/kg·K].

At the obtaining of the amorphous alloys, by rapid cooling, the viscous distortion energy must be lower in order to allow the particle to deform rapidly, the alloy viscosity increasing rapidly from 10^{-1}Pa·s to 10^{14}Pa·s during the passing from the overcooled liquid to the amorphous material. The superficial consumed energy for the particle's shape change, from spherical particle to flattened one must be higher because to the same material volume the sphere has the lowest surface from everyone. The inter-phasic reaction energy, of cohesion – adhesion is most likely to be higher in order to assure the link between layer and sub-layer. To the amorphous materials deposited by thermal spraying the link between layer and sub-layer is generally lower because the diffusion in the classic sense does not take place.

The accumulated energy under the shape of residual internal tensions may be bigger due to the solubility extension of the alloys in solid state by the saturation of the alloy basic network (the crystalline network is tensioned to the rapid cooling). The consumed energy in the flattened particle E_m, to the rapid cooling, is bigger comparing to a particle from the same alloy obtained in crystalline state.

3. THE ADHESION MECHANISMS AND PROCESSES

In the zone layer – interface – sub-layer it takes place the interaction between the particles deposited by thermal spraying and the sub-layer / basic material and from the individual flattened

particles it is formed a deposited layer, phenomena presented suggestively in the figures 1 and 2 [3,4].

The depositing by thermal spraying with plasma jet is a technological proceeding with material contribution where the layer comes into being by the incremental depositing of the particles thermal sprayed on the sub-layer and the increasing of the layer's thickness is rapid, but the process itself is stochastic.

The experimental and technical studies demonstrate that the flattening and the cooling on the sub-layer (fig.3) depend on: the particles' dimension before the impact, speed, melting parameters, roughness, temperature and reactivity of the sub-layer etc. Due to the great number of parameters, over 50 according to [1,2] and correlated between them it is difficult to study also the influence of the processes that took place at the forming of the deposited layers structure.
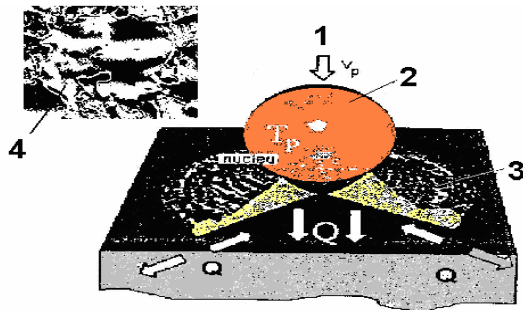
Figure 2. Distortion (theoretical/real) of the melted particle in the zone of sub-layer.

1- direction of particle's spraying; 2 – not deformed particle; 3 – theoretically deformed particle; 4 – really deformed particle.

The variation in time of the **particle's diameter** that is flattening is given by the relation (5) [2,3]:

$$d(\tau) = \xi \cdot d_p \cdot \sqrt{1 - \exp\left(-2\sqrt{3}\frac{1}{\xi} \cdot \frac{v_p}{d_p} \cdot \tau\right)}, \ [m] \qquad (5)$$

The radial expansion speed to the impact of the particle that is flattening is given by the relation (6) [2,3]:

$$v_{rad} = \frac{\sqrt{3}}{2} \cdot v_p \cdot \xi, [m/s] \qquad (6)$$

The impact time is defined as being the time when the particle with the speed v_p passes through the radial expansion a distance equal to the particle's beam r_p, and it is given by the relation (7) [2,3]:

$$\tau_c = \frac{d_p}{2v_p}, \ [s] \qquad (7)$$

The flattening time of the particle τ_f is given by the relation (8)[3] :

$$\tau_f = 1,14\xi\frac{d_p}{v_p}, \ [s] \qquad (8)$$

where: ξ- the flattening degree;

d_p – the particle initial diameter;

The physical nature of the adhesion is determined mainly by the forces Van der Waals, forces that action between the layer and sub-layer molecules determining the apparition of some pressures between the surfaces. These pressures are bigger to little distances of atomic distance order and decrease rapidly during the distance increasing. From this reason, in order to have a good adhesion it must be assured a perfect contact layer – sub-layer (the roughness must tend to zero).

The adhesion is determined by the following mechanisms and processes:

1. the mechanic mechanism of the layer – sub-layer, particle – particle, particle – inclusion adhesion;
2. the adhesion thermal mechanism;
3. the adhesion diffusive and chemical mechanism;
4. the influence of the oxidation processes;
5. the effect of the flattened particles morphology on the adhesion;
6. the influence of the remanent tensions on the adhesion.

The mechanic adhesion mechanism. The mechanic interaction between layer and sub-layer is produced because of the kinetic energy loss of the drops that heat the sub-layer. During the depositing by thermal spraying operation as a result it appears a great contact pressure of order of 100 MPa till 300 MPA that has an essential contribution to the forming of the layer – sub-layer link.
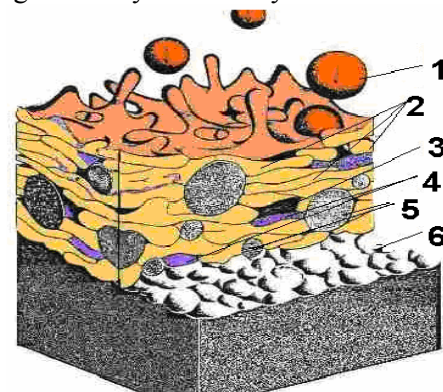
Figure 3. Forming of the layer by thermal spraying with plasma jet.

1 – the particle before impact ; 2 – lamellar flattened particles; 3 - pore; 4 – rusty particle; 5 - particle not melted; 6 – sub-layer.

The particle – sub-layer mechanic adhesion presented in the table 1 is explained by the fact that the particle in plastic state to impact is moulding on the sub-layer roughness and thus it is produced an anchoring effect. The thermal sprayed layer has usually a lamellar structure (fig. 3, point 2), the flattened particles adhesion between them by a blocking effect because of the mechanic interpenetration. The mechanic adhesion by interpenetration increases with the increase of the density, viscosity, drops speed and with the sub-layer roughness (fig. 3, point 6) and decreases with the increase of the superficial tension to the drop – sub-layer interface. This is maximal to the perpendicular thermal spraying on the sub-layer.

Table 1. Succession of the stages of the thermal sprayed layer forming

Particle	Thermal sprayed layer forming	Adhesion nature
	Pre-impact of the particle	-
	Impact of the particle with the sub-layer	Mechanic
	Beginning of the particle radial expansion	Mechanic, Metallurgic
	Particle radial expansion	Metallurgic
	Particle maximum radial expansion	Metallurgic superficial
	Particle solidification	Diffusive

2. The adhesion thermal mechanism. The local diffusion between particle and sub-layer and / or sub-layer local melting at the interaction with the melted particle comes into being to bigger adhesion. The thermal adhesion between layer and sub-layer takes place when the metallurgic adhesion conditions are fulfilled. This type of adhesion is favored by the temperature and the pressure in an analogue way with the under pressure welding in solid state. It may be said that in these conditions there are formed micro-junctions (links between the thermal sprayed layer and the sub-layer). The melting formed in the sub-layer may have the depth from 0,1μm to 10μm [4,9].

3. The adhesion diagrammatic diffusive mechanism. At the impact of the particle with the sub-layer it is created a big contact pressure that favor the diffusion between the particle liquid stage

and the sub-layer interface and the atoms from the sub-layer pass in the liquid stage of the flattened particle. This phenomenon is named inter-diffusion or reciprocal diffusion and takes long a very short time τ_s, (appreciatively 0,4μs) till the contact surface of the particle with the sub-layer passes in solid state.

The atoms diffusion depth may be determined with the relation (9) [9]:

$$d = 2\sqrt{D \cdot \tau_s} \, , \, [m] \qquad (9)$$

where: D is the diffusion coefficient, in [m³/s];

τ_s - time during the diffusion, in [s];

For a diffusion coefficient D = 10^{-9}m³/s, the atoms diffusion depth d = 0,2 nm [3,5].

4. The oxidized processes mechanism. The particles from the plasma jet are oxidizing because of the air entry in the thermal spraying jet or of the presence of the oxygen in the used gases. Also, the particles are oxidizing during the flattening and the solidification on the sub-layer that could oxidize because of the thermal / plasma jet radiation action. During the thermal spraying the oxides from the melted particles surface may mix because of the turbulence with the stages of the melted materials from other particles and stay in the layer after solidification. The presence of the oxides particles (fig. 3, point 4), modifies the heat transfer to the interface and between particles because of the thermal diffusion reduced coefficient. If the sub-layer temperature is too big, the sub-layer may oxidize, resulting a weak adhesion and a decreasing of the thermal transfer coefficient.

5. The flattened particles radial expansion morphology effect on the adhesion. The layer – sub-layer adhesion depends on the shape of the drop that is flattening (fig. 2, point 3 – the particle theoretical flattening; point 4 – the particle real flattening), as a result of the impact with the sub-layer. If the sub-layer is very cool than it takes place the under-cooling that on its turn initiates the solidification that develops in the drop because of the contact / impact pressure in the particle central zone. It results thus a more rapid solidification and a better adhesion in the center of the drop and it is in this case weaker. If the sub-layer has a relative big temperature, the thermal under-cooling is enough for the initiation of the solidification to the particle – sub-layer contact, thus resulting flattened drops with a radial regular expansion under the form of a disc that has a good adhesion to the sub-layer. A big roughness of the sub-layer hinders the flattening process and also the forming of the diffusive adhesion favoring thus the forming of links by mechanic and metallurgic adhesion.

6. The remanent tensions effect on the adhesion. The remanent tensions influence in a certain way the adhesion of the thermal sprayed layer to the sub-layer. Thus the micro – splits and / or the incipient splits spread along the interface due to the residual tensions and may interrupt the link of the sprayed layer with the sub-layer determining the exfoliation of the deposited layer. The apparition of the remanent tensions [5] owes of the inner properties of the material deposited by thermal spraying, the depositing or cooling depositing proceeding, the elasticity (dilatation / contraction) and thermal coefficients different from layers and sub-layers.

Theoretically there may be deposited as many layers as it is wanted, but practically the exfoliation produces due to the internal residual tensions actions [4], due to the tensions applied from the exterior and to these that appear in exploitation. The residual tensions may have an important role in the increasing of the resistance to exfoliation by the inhibition of the initiation interfacial micro – splits producing or by the fact that the external tensions oppose or because the tensions result is little than the tension necessary for the layer exfoliation.

4. EXPERIMENTAL RESERACHES ON THE ADHESION OF THE SUPERFICIAL LAYERS OBTAINED FROM AMORPHOUS ALLOY OF TYPE NiCr

The notion of adhesion is used also in the sense of a mechanic characteristic of the deposited layer defined as being equal with the force necessary for the detachment of a deposited layer that has a unitary surface.

The covering by thermal projection with the alloy that contains NiCrFeSiBCY is a dynamic process and from this reason there is no rigorous modeling of the depositing processes.
There is no standard concerning the covering devices and the characteristics of the deposited layers, so it may be not used any layer as reference and any layer could not be totally reproduced.
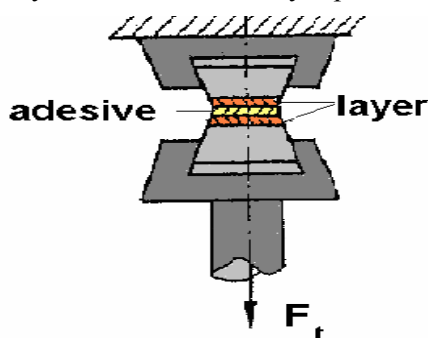

Figure 4. Scheme of the device for determining the adhesion to traction

The scheme of the adhesion to traction determining device is presented in the figure 4. The basic condition for this test is that the detachment does not produce in the adhesive layer.

The establishing of the adhesion to bending is made with the device presented in the figure 5. It is determined the force when it appear firstly the splits in the deposited layer, the shaft s and the bending angle α [3].

Because the deposited layers by thermal spraying with plasma jet to an atmospherically pressure had a little thickness (20-300μm), it was made the adhesion determining by the tests to traction and bending.

In order to realize tests by traction there were deposited layers by thermal spraying on 20 essays. The adhesive used to the determining of the adhesion to traction is of type "bisonite" with the maximal resistance to fracture of 16 000 Pa.
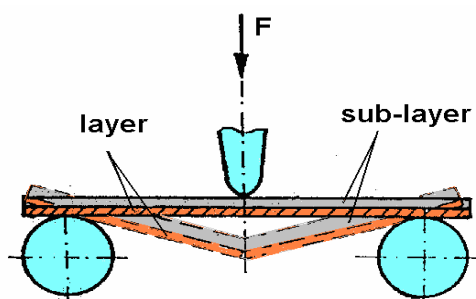

Figure 5. Scheme of the device for the determining the adhesion to bending

For determining the adhesion to bending (fig.5) there were used samples with square section of rolled steel having the following dimensions: 140 x 10 x 10 mm. The distance between the bearings was l = 120 mm, their diameter was D = 30 mm and the part bend shaft was s = 15 mm. The loading is made applying a force F that produces an unitary effort to bending of $10\left[\dfrac{N}{m^2 \cdot s}\right]$, till the apparition of the first split. The measures' obtained results are presented in the tables 2 and 3.

Table 2. Experimental values obtained to traction

Adhesion to traction		
S x10 [6], în m^2	F$_t$, in N	σ_t x10 [6], in N/m^2
99.8	110	1,1
101,1	420	4,6
98,2	280	3,8
99,2	560	5,6
99,4	460	4,6
98,8	360	3,6
100,2	480	4,8
100,1	480	4,6
99,6	360	2,6
98,6	480	4,8

Studying the data from the tables 2 and 3 it may be observed that the adhesion values obtained to the traction test are not big comparing to the adhesion values obtained to bending test and the obtained results are in a large interval.

The causes that could affect the deposits adhesion are:

The send – blasting of the sub-layer in made on purpose for a little roughness and in order to allow the flattening / the radial expansion of the particles in fluid state and as a result the mechanic adhesion of the particles to sub-layer is little;

Table 3. Experimental values obtained to bending

Adhesion to bending		
F_t, in N	$s \times 10^6$, in m	α, in grd
2600	4,00	7,80
3000	8,60	16,6
3100	9,80	18,6
3600	11,6	20,8
3200	10,2	19,6
3600	7,40	21,6
3500	12,6	19,8
3600	12,0	14,6
3200	12,6	22,6
3600	8,80	26,0

The sub-layer anti – adhesion forces generated by the residual tensions due to the rapid cooling of the particles are not compensated by the little roughness of the sub-layer;

The adhesion of the layer thermal sprayed to sub-layer is a mechanic one and less a metallurgic or diffusive one.

The adhesion of the layer deposited to the bending test was made by measuring the shaft s and the bending angle α, till the apparition of the first split in the layer.

The layers obtained by spraying with plasma jet are submitted to bending surpassing the elastic deformation zone. The force F is the pressing force till the apparition of the first split in the deposited layer (table 5.3). The shaft s and the bending angle α to which appear the first splits in the thermal sprayed layer represent the measure of depositing lamellar cohesion and not the measure of the adhesion of the sprayed layer to the sub-layer.

The final conclusion is that the adhesion is good enough, thus the deposited layers by thermal spraying may be worked mechanically and with them may be reconditioned / covered preventively parts that work in not so severe exploitation conditions from the current production.

5. CONCLUSION

The adhesion of the layer thermal sprayed to sub-layer is a mechanic adhesion and less a metallurgic or diffusive one.

The adhesion values obtained to the traction test are not so big comparing to the adhesion values obtained to the bending test and the obtained results are in a large interval.

The adhesion is enough good thus these layers resistant to wear and corrosion may be worked mechanically and with them may be reconditioned / covered preventively parts that work in not so severe exploitation conditions form the current production.

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