



Serbian Tribology  
Society

# SERBIATRIB '13

13<sup>th</sup> International Conference on  
Tribology



Faculty of Engineering  
in Kragujevac

Kragujevac, Serbia, 15 – 17 May 2013

## THE INFLUENCE OF CORROSION ON THE MICROSTRUCTURE OF THERMALLY TREATED ZA27/SiC<sub>p</sub> COMPOSITES

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**Abstract:** *The influence of corrosion on the microstructure of ZA27/SiC<sub>p</sub> composites was examined. The composites were produced by compo casting technique and then subjected to the thermal treatment (T4 regime). Microstructural examinations were performed after 30-day exposure of thermally treated composites in the sodium-chloride solution. Corrosion processes have occurred in the composite matrix. Corrosion did not affect SiC particles in the composites. The local progress of corrosion in depth of the composite matrix was noticed in micro-cracks. Corrosion resistance of ZA27/SiC<sub>p</sub> composites was evaluated based on the mass loss of composite samples during the immersion test. It was found that corrosion resistance of the composites decreased with increase in content of SiC particles. The applied thermal treatment had a negative influence on the corrosion resistance of ZA27/SiC<sub>p</sub> composites.*

**Keywords:** *Metal-matrix composites, ZA27 alloy, Compo casting, Thermal treatment, Corrosion, Microstructure*

### 1. INTRODUCTION

Domestic composites with base ZA27 alloy [1, 2] have been developed with an aim to obtain composites which maintain good mechanical characteristics at elevated temperatures as well as to make composites with improved tribological properties compared to those of the matrix alloy. Particulate ZA27/SiC<sub>p</sub> composites were shown to possess significant tribological potential because of high hardness and high wear resistance [3, 4]. Within this work, domestic ZA27/SiC<sub>p</sub> composites were obtained by compo casting technique. The matrix alloy, with 27 wt. % aluminum, belongs to zinc–aluminum foundry alloys with relatively high

content of aluminum (ZA alloys). The alloy is characterized by good physical, mechanical and technological properties (low density, high strength and hardness, easy machinability) [5, 6], by a substantial resistance to corrosion and high wear resistance [7–9]. This enabled commercial application of ZA27 alloy as a significant tribomaterial, especially for making bearings and bushings.

ZA27 alloy solidifies in the wide temperature range and is suitable for processing in the semi-solid state [10]. This led to the application of compo casting technique for producing domestic particulate composites with base of ZA27 alloy. Micro-particles of SiC [1], Al<sub>2</sub>O<sub>3</sub> [1, 2, 11, 12], graphite [9, 13] or ZrO<sub>2</sub> [14] were incorporated in the semi-

solid melt of ZA27 alloy using mechanical mixing. Obtained composites were subjected to microstructural examinations [11, 12] and tribological tests [9, 13]. In addition, mechanical characteristics of the composites have been studied, at room temperature [11, 12] and moderately elevated temperatures [2]. However, corrosion behavior of domestic composites with base ZA27 alloy has not been tested so far.

Physical, mechanical and corrosion characteristics of metal-matrix composites are deeply influenced by the microstructure of metal matrices [15, 16]. It was shown that thermal treatment affected the microstructure and properties of ZA27 alloy [17–19]. A beneficial effect of T4 regime on ductility [17] and tribological characteristics of ZA27 alloy [18, 19] was noticed, although this thermal treatment resulted with minor reduction in hardness and tensile strength [18]. In addition, it was shown that T4 regime affected the microstructure and corrosion resistance of as-cast ZA27 alloy [20] and thixocast ZA27 alloy [21].

ZA27 alloy is highly corrosion resistant in atmospheric conditions and natural waters [22]. The most common form of corrosion in these environments is general corrosion, which enables calculations of the alloy corrosion rate, based on the weight loss of samples during exposure in corrosive media. Immersion tests in chloride solutions have been used frequently, because chloride ions are present in numerous corrosive environments.

Thixocast ZA27 alloy is the base of ZA27/SiC<sub>p</sub> composites obtained by compo casting technique [23]. Accordingly, the microstructure of thixocast alloy is actually the microstructure of the composite matrix. It was shown recently that thermal treatment (T4 regime) negatively affected the corrosion behavior of thixocast ZA27 alloy [21]. However, there have been no published results until now, concerning the effect of T4 regime on the microstructure and corrosion resistance of ZA27/SiC<sub>p</sub> composites obtained by compo casting technique.

Considering the importance of corrosion resistance for selection and application of metal-matrix composites, it was the aim of this

work to study the influence of corrosion on the surface appearance and microstructure of the thermally treated ZA27/SiC<sub>p</sub> composites. Corrosion resistance of the composites was evaluated based on the weight loss of samples during immersion in the sodium-chloride solution.

## 2. EXPERIMENTAL

### 2.1 Materials

A domestic producer of zinc-aluminum alloys (RAR Foundry<sup>®</sup> Ltd., Batajnica) has provided the master alloy for the experimental work. SiC particles (with average diameter of 40 μm) were obtained from the domestic manufacturer of abrasive products (Ginić Tocila<sup>®</sup> Ltd., Barajevo).

ZA27 alloy was conventionally melted and casted in the Department of Materials Science "Vinča" Institute. Chemical composition of the alloy is given in Table 1.

**Table 1.** Chemical composition of ZA27 alloy

Element*	Al	Cu	Mg	Zn
wt. %	26.3	1.54	0.018	balance

\*Concentration of other elements (Fe, Sn, Cd, Pb) is within acceptable limits.

Compo casting technique was used for making composites with 1, 3 and 5 wt. % SiC particles. The particles were incorporated into the semi-solid melt of ZA27 alloy with use of mechanical mixing. Parameters of the applied compo casting aprocess nd description of the apparatus can be found in [23].

Composite castings were subjected to a hot pressing, in order to reduce porosity and improve the bond strength between the matrix and particulate reinforcements. Samples for microstructural examinations and corrosion testing were machine cut from the composite castings. The samples were thermally treated according to T4 regime: solutionizing at 370°C for 3 hours, with subsequent water quenching and natural aging.

## 2.2 Methods

### Microstructural examinations

Surface morphology and microstructure of thermally treated ZA27/SiC<sub>p</sub> composites were examined by optical microscopy (OM) and scanning electron microscopy (SEM). Carl Zeiss optical microscope and JEOL JSM-5800 scanning electron microscope were used. Cylindrical samples (5 mm in diameter and 8 mm in height) were embedded in the polymethacrylate and then they were ground and polished. Wet grinding was performed with successively finer abrasive papers (240, 360, 600 and 800 grit SiC), while polishing was done using polishing cloth and diamond paste (particles size up to 2 μm). Aqueous solution of nitric acid (9 v/v % HNO<sub>3</sub>) was used for etching of the samples.

The samples were rinsed with acetone and dried in the air before exposure in the test solution (3.5 wt. % NaCl). After finishing of the exposure, the samples were prepared for metallographic examination in the usual way.

### Corrosion rate testing

Corrosion rates of thermally treated ZA27/SiC<sub>p</sub> composites were calculated based on the samples mass loss during exposure in the test solution (immersion test). Preparation of the samples and testing procedure were performed in accordance with ASTM G31 [24]. The samples (18 x 28 x 3 mm), in triplicate, were suspended vertically in the stagnant sodium-chloride solution (3.5 wt. % NaCl, pH=6.7) open to the atmosphere. The test was performed at room temperature (23 ± 2°C). After 30 days of exposure, the samples were withdrawn from the test solution and rinsed with distilled water. Corrosion products were removed from the surface of the samples by chemical procedure [25]. The samples were then reweighed to determine the mass loss during exposure in the test solution.

Calculation of the average corrosion rate *CR* [mm/year] is based on the mass loss of the samples  $\Delta m$  [g] during the immersion test:

$$CR = \frac{8.76 \cdot \Delta m}{d \cdot A \cdot \tau} \quad (1)$$

$\tau$  is the exposure time (720 hours),  $A$  is the sample surface [cm<sup>2</sup>] and  $d$  [g/cm<sup>3</sup>] is the

composite density. Values of the composite density (for the composite with 1, 3 and 5 wt. % SiC particles, respectively) were calculated [23] and shown in Table 2.

**Table 2.** Density of ZA27/SiC<sub>p</sub> composites

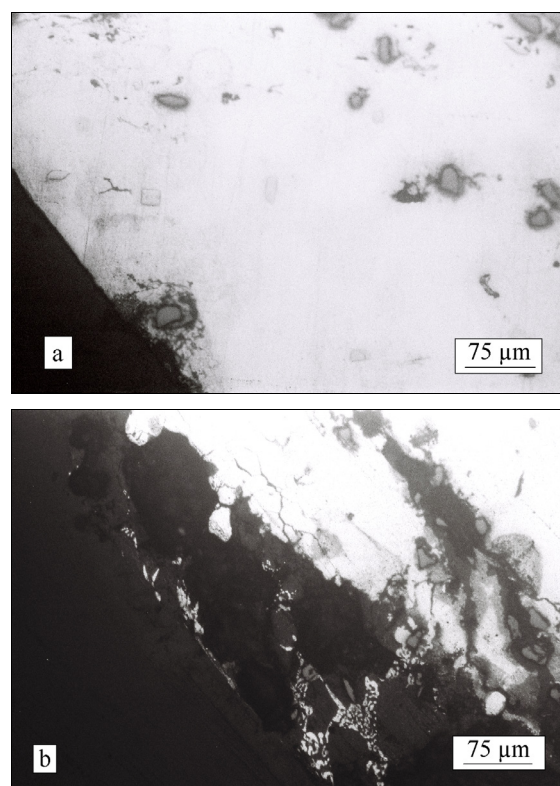
Material	ZA27/1%SiC <sub>p</sub>	ZA27/3%SiC <sub>p</sub>	ZA27/5%SiC <sub>p</sub>
$d$ [g/cm <sup>3</sup> ]	4.97	4.92	4.87

The values in Table 2 were used to calculate corrosion rates of the thermally treated ZA27/SiC<sub>p</sub> composites.

## 3. RESULTS AND DISCUSSION

### 3.1 Microstructure of thermally treated ZA27/SiC<sub>p</sub> composites

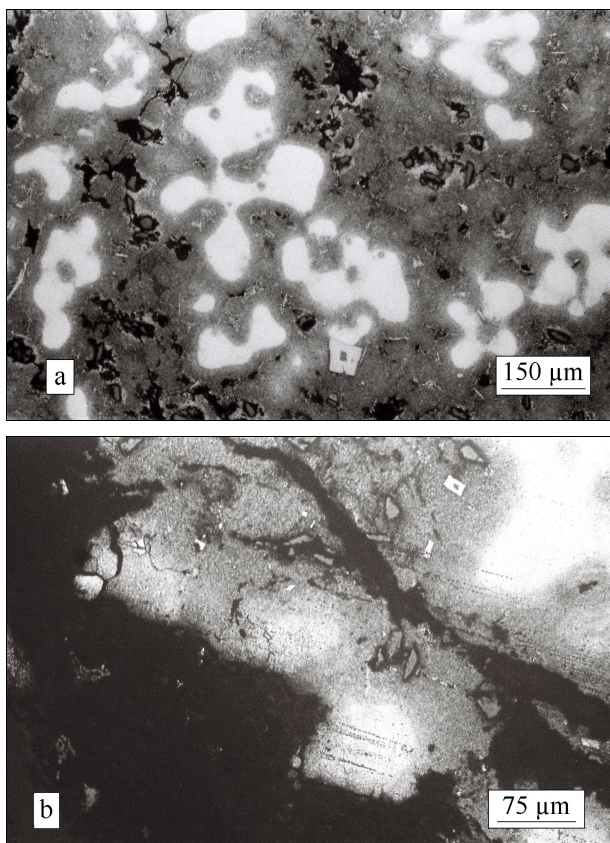
Surface appearance and microstructure of thermally treated ZA27/SiC<sub>p</sub> composites were examined before exposure and after 30-day exposure in the sodium-chloride solution. Surface appearance of the composites with 3wt. % SiC particles, is shown in Figure 1a, b.



**Figure 1.** Surface appearance of the thermally treated composite ZA27/3wt.%SiC<sub>p</sub> (OM, polished): a) before exposure, b) after 30-day exposure in 3.5 wt.% NaCl.

SiC particles are uniformly distributed in the metal matrix (Fig. 1a). A few inclusions can be noticed on the surface of the composite sample and mechanical damages on the edge of the sample. Applied thermal treatment had no effect on the particles of reinforcement and their distribution in the composite matrix.

The microstructure of composites was revealed by etching (Figure 2a, b). It can be seen in Fig. 2a that SiC particles are distributed in the regions of  $\eta$  phase and regions of phase mixture  $\alpha+\eta$ . There are no voids, due to the fallout of SiC particles from the composite base (e.g. during machining or metallographic preparation of samples). This indicates good bonding between SiC particles and the matrix alloy.



**Figure 2.** Microstructure of the thermally treated ZA27/3wt.%SiC<sub>p</sub> composite (OM, etched): a) before exposure, b) after 30-day exposure in 3.5 wt.% NaCl.

Main micro-constituents in the composite matrix are also visible in Fig. 2a. The microstructure of the composite base is non-dendritic and is characterized by the presence of large primary particles [21, 23]. The primary particles are complex; they consist of a core (rich in aluminum) and a periphery (composed of the phase mixture  $\alpha+\eta$ ). Interdendritic  $\eta$

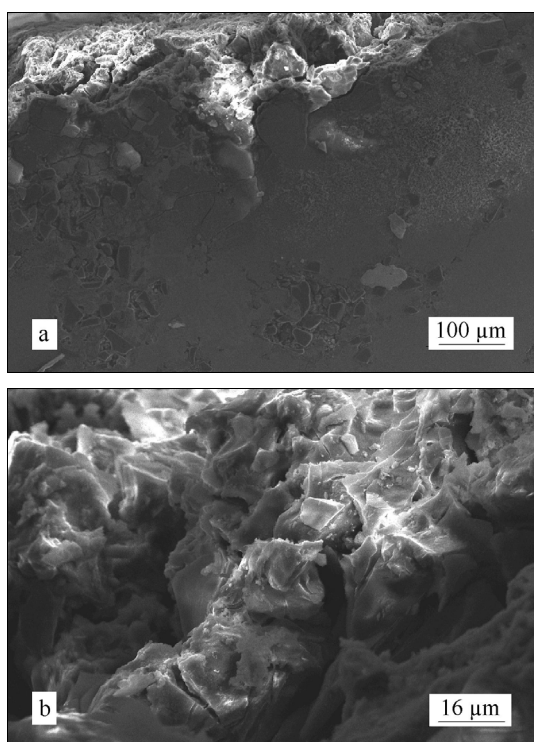
phase, rich in zinc, is located between the primary particles. The microstructure of the composite matrix and the microstructure of thixocast ZA27 alloy are morphologically very similar [23]. The applied thermal treatment (T4 regime) has caused changes in the structure of the composite matrix. The region of phase mixture  $\alpha + \eta$  was expanded, while the regions of individual phases ( $\alpha$  and  $\eta$ ) were reduced. In addition, the size of primary particles of  $\alpha$  phase was decreased for about 30 vol. % [21, 23]. All this resulted with finer microstructure of the composite matrix. However, the increase in number of micro-cracks on the phase boundaries  $\eta/\alpha+\eta$  was noticed in the composite matrix after the thermal treatment [23]. Thermal stress at boundary surfaces matrix/particle, due to quenching within thermal treatment, was preceded by thermal stress during solidification of the composite mixture. The stress can cause a local deformation of the metal matrix around particles of reinforcement [26], appearance of micro-cracks or fracture of the particles. Electrolytes can be retained in the micro-cracks, causing local progress of corrosion processes into depth of the composite base.

The number of boundary surfaces matrix/particle was significantly increased in the ZA27/SiC<sub>p</sub> composites due to the presence of SiC particles.. It can be assumed that dislocation density was also increased during cooling of the composite mixtures, due to different coefficients of linear expansion of the matrix ZA27 alloy and SiC particles.

Corrosion processes have influenced the surface appearance and microstructure of thermally treated ZA27/SiC<sub>p</sub> composites. The surface appearance of the composites with 3 wt. % SiC<sub>p</sub>, after 30-day exposure in the sodium-chloride solution, is shown in Fig. 1b. Large primary particles of  $\alpha$  phase are visible in the central area of the composite sample. It can be seen that corrosion has started at places of mechanical damages, voids, inclusions. Corrosion processes occurred in the composite base, in the regions of phase mixture  $\alpha+\eta$  and regions of  $\eta$  phase. The local progress of corrosion was noticed in the micro-cracks and pores. The micro-cracks were probably formed during solidification of the composite mixtures, in hot pressing as well as during quenching

within thermal treatment of the composites. The presence of micro-cracks negatively affected corrosion resistance of thermally treated ZA27/SiC<sub>p</sub> composites.

SiC particles were not involved in corrosion processes because of their inherent chemical stability. However, these particles have influenced corrosion behavior of ZA27/SiC<sub>p</sub> composites. The continuity of boundary surfaces matrix/particle is disturbed in the clusters of SiC particles. On these places micro-pores and micro-cracks can be formed. Due to the retention of sodium-chloride solution in these places, local progress of corrosion in depth of the composite matrix was noticed, as it was mentioned before.



**Figure 3.** Corrosion products of the of thermally treated ZA27/3wt.%SiC<sub>p</sub> composite after 30-day exposure in 3.5 wt.% NaCl (SEM): a) surface appearance, b) detail.

During exposure in the sodium-chloride solution, corrosion products were formed on the surface of the composite samples. Spongy, white deposits of the corrosion products, mostly in the form of rosettes, are shown in Figure 3a, b.

Microstructural examinations of thermally treated ZA27/SiC<sub>p</sub> composites, after exposure in the sodium-chloride solution, made it possible to gain some insight into the influence of corrosion processes on the structure of these composite materials. It was found that corrosion started in places of mechanical

damage, voids, inclusions. Corrosion processes have occurred mainly in the composite base, although in pores and micro-cracks, the local progress of corrosion in depth of the composites was noticed. Corrosion processes did not influence SiC particles.

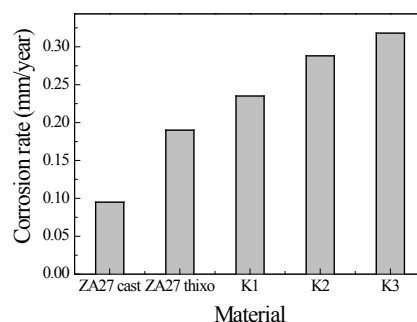
Results of the microstructural examinations, after exposure of thermally treated ZA27/SiC<sub>p</sub> composites in the sodium-chloride solution, are in accordance with results obtained during the immersion test.

### 3.2 Corrosion rate of thermally treated ZA27/SiC<sub>p</sub> composites

After finishing of exposure in the NaCl solution, corrosion products were removed from the surface of ZA27/SiC<sub>p</sub> composite samples by chemical procedure [25]. It was found that corrosion attack was mostly uniform, while corrosion processes took place predominantly on the composite surface. The average value of corrosion rate CR [mm/year] was calculated based on the mass loss of composite samples during the immersion test. The results are presented in Figure 4.

For the purpose of comparison, results of the immersion test for thermally treated ZA27 alloys (as-cast and thixocast) [21, 23] are also presented in Figure 4. It can be seen that corrosion rates of the composites are higher than those of both ZA27 alloys (as-cast and thixocast).

Corrosion resistance of the composite matrix (thermally treated thixocast ZA27 alloy) is higher than that of thermally treated composites.



**Figure 4.** Corrosion rate of thermally treated ZA27 alloys and ZA27/SiC<sub>p</sub> composites after 30-day exposure in 3.5 wt.% NaCl. K1 - ZA27/1wt.%SiC<sub>p</sub>, K2 - ZA27/3wt.%SiC<sub>p</sub>, K3 - ZA27/5wt.%SiC<sub>p</sub>.

Corrosion rate of thermally treated ZA27/SiC<sub>p</sub> composites increases with increase in content of SiC particles, because of increase

in number of micro-cracks and clusters of SiC particles. All above presented indicates lower corrosion resistance of thermally treated ZA27/SiC<sub>p</sub> composites with higher content of particulate reinforcements.

#### 4. CONCLUSIONS

Particulate ZA27/SiC<sub>p</sub> composites (with 1, 3 and 5 wt.% SiC particles) were obtained by compo casting technique and subsequently subjected to the T4 thermal treatment. Thermally treated composites were exposed in the sodium-chloride solution for 30 days. The influence of corrosion on the surface appearance and microstructure of the composites was examined. Corrosion resistance of the composites was evaluated based on the mass loss of composite samples during the immersion test. According to the results presented, the following conclusions can be proposed:

1. SiC particles are uniformly distributed in the metal matrix of the particulate ZA27/3wt.%SiC<sub>p</sub> composite that was made by compo casting technique.
2. Morphological changes and appearance of micro-cracks in the microstructure of the composite matrix were noticed after T4 thermal treatment. However, the thermal treatment had no effect on SiC particles and their distribution in the composite matrix.
3. Corrosion process has influenced the microstructure and surface appearance of thermally treated ZA27/SiC<sub>p</sub> composites, after 30-day exposure in the sodium-chloride solution. However, corrosion did not affect SiC particles in the composites.
4. Corrosion started at places of mechanical damages, voids, inclusions. Corrosion processes occurred mainly in the composite matrix although the local progress of corrosion was noticed in the micro-cracks.
5. Corrosion resistance of the composite matrix is higher than that of ZA27/SiC<sub>p</sub> composites.
6. Corrosion rate of thermally treated ZA27/SiC<sub>p</sub> composites increases with increase in content of SiC particles.
7. Applied thermal treatment (T4 regime) has shown a negative effect on the corrosion resistance of ZA27/SiC<sub>p</sub> composites.

#### ACKNOWLEDGEMENTS

The Ministry of Education, Science and Technological Development of the Republic of Serbia has supported financially this work through the projects TR 35021 and OI 172005. The authors are gratefully acknowledged to the RAR<sup>®</sup> Foundry Ltd., Batajnica (Belgrade, Serbia) and Ginić Tocila<sup>®</sup> Abrasive Products Factory Ltd., Barajevo (Belgrade, Serbia), for providing the master alloy and SiC particles, to perform this research.

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