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CORROSION OF Al/SiC METAL-MATRIX COMPOSITES

KOROZIJA KOMPOZITOV Al/SiC

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Discontinuously reinforced (DR) Al/SiC metal-matrix composites (MMCs) are modern, lightweight materials which have a very attractive combination of material properties and price. The use of DR Al/SiC MMCs is mostly limited to the military and aerospace, however, these materials are now beginning to penetrate civilian applications. Besides the mechanical behavior, a knowledge of the corrosion resistance of DR Al/SiC MMCs is very important, and so the corrosion resistance of Al/SiC composites has been investigated and discussed in comparison with a conventional Al alloy of similar composition. The results of the investigation show that the conventional unreinforced AlSi7Mg1 alloy has a better corrosion resistance in both the selected corrosion media. The best corrosion resistance is obtained in a 3.5 % water solution of NaCl: a corrosion medium that is comparable with aggressive sea water. Corrosion-resistance investigations showed that corrosion cracking did not occur as a result of stress corrosion. Only general surface corrosion was observed, which is reflected in a significant reduction in the area of the investigated samples. The reduction in area is a consequence of hydrogen embrittlement.

Key words: discontinuously reinforced Al/SiC metal-matrix composites, corrosion testing and behavior

Kompoziti vrste Al/SiC so moderni materiali, ki imajo v primerjavi z današnjimi konvencionalnimi materiali najboljšo kombinacijo masa-lastnosti-cena. Vendar je njihova uporaba zaenkrat omejena predvsem na vojaške in vesoljske tehnologije oziroma materiale. Ti materiali pa počasi prodirajo tudi na civilno področje in že zamenjujejo različne konvencionalne materiale v velikoserijskih proizvodnjah, kot so na primer avtomobilska industrija, bela tehnika, proizvodnja športnih izdelkov, izdelkov za prosti čas itd. Poleg mehanskih lastnosti je zato zelo pomembno poznavanje korozijske odpornosti te vrste materialov. Tako smo v laboratoriju za korozijo IMT v Ljubljani izvedli korozijske preiskave izbranega kompozita Al/SiC v iztiskanem in toplotno obdelanem stanju. Kot primerjava nam je rabila konvencionalno izdelana Al-zlitina podobne sestave. V prispevku predstavljamo potek in rezultate preiskav. Ti so pokazali, da ima konvencionalna zlitina AlSi7Mg1 boljšo odpornost proti koroziji. Najboljšo odpornost proti koroziji oziroma najmanjšo korozijsko hitrost imata oba izbrana materiala v toplotno obdelanem stanju in v 3,5 % vodni raztopini NaCl, ki najbolje opisuje agresivne razmere v obmorski atmosferi. Napetostno korozijske preiskave pri predpisanih obremenitvah niso pokazale, da bi prišlo do napetostnega korozijskega pokanja materialov. Prišlo je le do splošne površinske korozije, ki se izraža v občutnem zmanjšanju preseka (kontrakciji) preizkušancev. Zmanjšana kontrakcija preizkušancev glede na izhodno stanje je predvsem posledica vodikove krhkosti.

Ključne besede: neprekinjeno ojačani kompoziti vrste Al/SiC, korozijske preiskave

1 INTRODUCTION

Al-alloy-based matrix composites reinforced with ceramic particles (particularly with Al_2O_3 and SiC particles, platelets or whiskers) are modern, lightweight materials which have a very attractive combination of material properties and price. It is expected that in the near future these materials will begin to substitute for conventional structural materials in mass production, particularly in the automotive and other transport industries. These materials have also begun to substitute conventional materials in household appliances, computers, audio and video equipment, as well as in sport and leisure applications.

Different manufacturing routes for DR Al/SiC MMCs have been developed, these include the direct incorporation of relatively large particle reinforcement (SiC particles, platelets or whiskers) into the molten Al alloy, the infiltration of SiC preforms with molten Al alloy and using powder metallurgy (PM) procedures. PM DR Al/SiC MMCs usually have better mechanical properties than those prepared by the casting procedures because they contain a very uniform dispersion of small particles or whiskers in the metal matrix. The Al alloy powder is produced by rapid-solidification technology (atomisation) and so PM DR Al/SiC MMCs also have a better chemical and microstructural homogeneity of the metal matrix. These materials are, however, rather expensive. The most promising and probably the cheapest industrial manufacturing procedure is the direct incorporation of relatively large (10-60 μm) SiC particles into molten Al alloy during vertical continuous (D.C.) casting of billets/ingots. This procedure has already been developed on the industrial scale[1-3].

The addition of a non-metallic phase or reinforcement into the metal matrix increases the yield strength of the composite. Compressive and tensile strengths, as well as the hardness at room and elevated temperatures, are also increased significantly, resulting in an improvement in the wear resistance of the composite material. With the addition of the SiC reinforcement the Young's modulus of elasticity and the thermal expansion coefficient are also improved. Unfortunately, with the increased content of reinforcement in the metal matrix the ductility (fracture toughness, tensile-test elongation and reduction in area) is considerably reduced. In addition, a big disadvantage of Al/SiC MMCs is their poor machinability[4-5], and their corrosion resistance might also be problematic. The SiC particles in the metal matrix serve as active cathodes and tend to reduce corrosion resistance of the metal matrix. Therefore, the aim of this work was to investigate the corrosion behavior of a selected Al/SiC composite in comparison with an unreinforced material (Al-alloy AlSi7Mg1 type) of a similar chemical composition. For the investigations, a D.C. cast, extruded and heat-treated Al/SiC composite with approximately 20 vol.% of SiC particles was selected[6-7]. Chemical compositions of the metal-matrix composite and the Al alloy are given in **Table 1**.

Table 1: Chemical compositions of Al/SiC metal-matrix composite and Al alloy

Tabela 1: Kemična sestava kovinske osnove kompozita Al/SiC in primerjalne Al zlitine

Material	Chemical composition (weight %)							
	Si	Fe	Cu	Mg	Ni	Ti	Mn	Al
Al/SiC	7.2	0.10	0.008	0.48	0.007	0.079	0.004	balance
AlSi7Mg1	10.0	0.25	0.024	0.32	0.010	0.008	0.010	balance

As shown in **Table 1**, the real chemical composition of the selected Al alloy deviates from the specification. The real composition of the Al alloy corresponds to AlSi10Mg0.5. A deviation in Si content (8.8 - 9.5% Si) is also observed in the Al/SiC composite.

2 TESTING METHODS

2.1 Laboratory determination and testing of the general corrosion resistance

The laboratory testing of corrosion resistance for metals and their alloys is standardized all over the world. The successful forecast of corrosion resistance, however, depends on the possibility of simulating the real corrosion conditions. The electrochemical corrosion testing methods are usually based on potentiodynamic measurements which make it possible to establish different corrosion parameters during combined potential-current activity .

The measure of the corrosion rate is the corrosion electrical current, the mass of corroded metal being proportional to the rise in electric charge during the relaxation of valence electrons by the anode reaction of metal oxidation ($M \rightarrow M^{n+} + ne^-$). **Figure 1** shows a typical experimental set-up. The main parts of the apparatus are the potentiostat, the corrosion cell with working electrode dipped into the corrosion medium, two auxiliary electrodes, a calomel's electrode, a computer and printer. All corrosion investigations were performed with this kind of apparatus, manufactured at EG-G PAR using Softcorr-352 software.

Figure 1: Electro-chemically-based determination of corrosion resistance using EG-G PAR potentiostat 273 and Softcorr-352 software (Corrosion Lab, Institute of Metals and Technology, Ljubljana, Slovenia)

Slika 1: Elektrokemično določanje korozijske odpornosti z uporabo EG-G PAR-potenciostata 273 in Softcorr-352

2.2 Laboratory assessment of stress-corrosion cracking

Stress-corrosion cracking (SCC) is a measure of the degradation of structural materials during slow crack propagation. The crack is formed in a particular environment as a result of mechanical stresses and corrosion. The stresses for SCC are small, and in most cases smaller than the yield strength of the material. They are the result of the external load of the construction or its structural elements, and can often be the consequence of machining or welding. The cracks are formed perpendicularly to the load direction and can cause a sudden catastrophic fracture of the structural element or even a total break in the structure. These effects cannot be predicted by classical fracture mechanics and so it is necessary to know the real environmental conditions because the correct selection of material for a given application can significantly

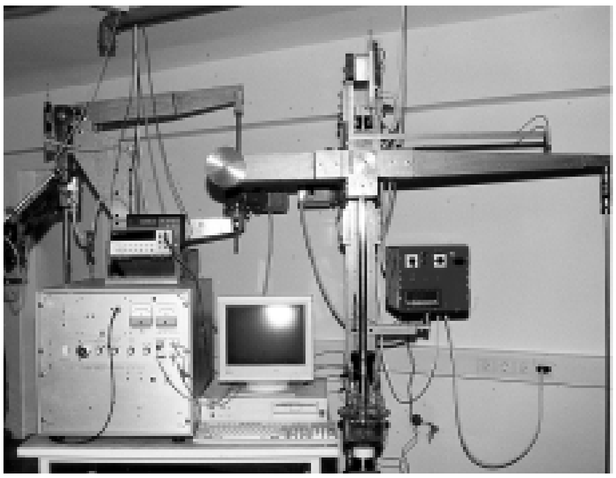

Figure 2: Laboratory equipment for anode and cathode electro-chemical polarization of statically loaded samples

Slika 2: Laboratorijska oprema za anodno ali katodno elektrokemično polarizacijo statično obremenjenih vzorcev decrease the risk of SCC and its catastrophic consequences.

SCC can occur via several different mechanisms. It is well known that Al alloys are prone to anode SCC in chlorine media. Therefore, an anode polarization of selected samples was performed using the method shown in **Figure 2**. In this way, the anode mechanism of SCC has been established.

3 RESULTS AND DISCUSSION

3.1 Electrochemical corrosion investigations

Electrochemical corrosion measurements give a basic picture of the corrosion behavior of material in a particular corrosion medium. Anode polarization curves give the basic information as to whether the material was in the active or passive state and if the corrosion continued or the material was passivated by the formation of a thin protective layer.

The measurements were performed in distilled water and for ten minutes in air pre-blown water. In this way an oxidising medium was prepared and the oxidation of the investigated material was made possible. This medium is normally used for the simulation of an unpolluted wet air atmosphere. Electrochemical measurements were also performed in a 3.5% water solution of NaCl. This solution is relatively aggressive and causes intensive corrosion. This medium simulates aggressive atmospheric conditions similar to a sea-water atmosphere.

The experiments showed that the selected materials ware not passivated in either media. Therefore, the measurements of corrosion rate with the method of Taffel's recording of polarization were also performed. The results of these experiments are given in **Table 2** and shown in **Figures 3** and **4**.

Table 2: Results of electro-chemical measurements of corrosion rates
Tabela 2: Rezultati elektrokemičnih meritev korozijskih hitrosti

Material	Material state	Corrosion rate (mm/year)	
		H_2O aired	3.5 % NaCl
AlSi7Mg1	extruded	0.035	0.055
	heat treated (T6)	0.025	0.002
Al/SiC	D.C. + extruded	0.056	0.060
	heat treated (T6)	0.055	0.011

For both selected corrosion media the anode potentiodynamic curves given in **Figures 3** and **4** show that the shape of the anode part of the curves are steep and that the passivation of the materials was not possible meaning that an active corrosion occurred. However, all systems are shifted towards low current densities and, therefore, the calculated corrosion rates are small (see **Table 2**).

It is clear from the curves given in **Figure 1** that the Al/SiC composite has a lower corrosion resistance than the AlSi7Mg1 alloy. This lower corrosion resistance can be ascribed to its microstructure which consist of a fine dispersion of SiC particles in an Al-alloy-based matrix. These fine carbide particles serve as active cathodes and promote the solution of the Al-alloy-based matrix. The tendency for an increasing corrosion rate was observed for both media, as well as for both as-extruded and heat-treated alloys.

From the corrosion investigations performed on both alloys in two different corrosion media (aired and salt water) it can be concluded that in all cases the corrosion rate is relatively low, however, it is a little larger for the Al/SiC composite because of its two-phase microstructure. Nevertheless, it is clear that both alloys are corrosion resistant in the selected corrosion media under both conditions. (**Figure 5**).

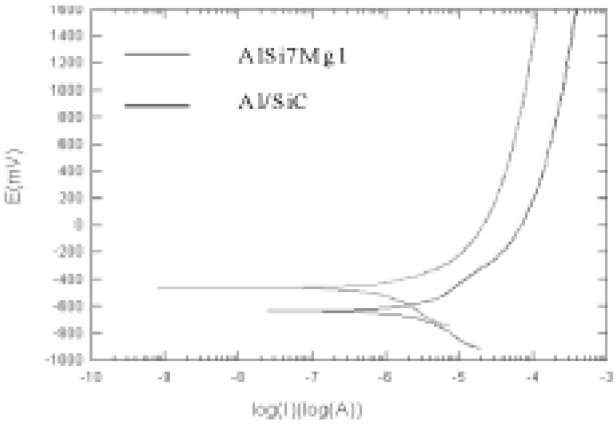

Figure 3: Curves of anode potentio-dynamic polarization for the extruded Al/SiC MMC and the AlSi7Mg1 alloy in distilled water
Slika 3: Anodna potenciodinamična polarizacija ekstrudiranega kompozita Al/SiC in ekstrudirane zlitine AlSi7Mg1 v destilirani vodi

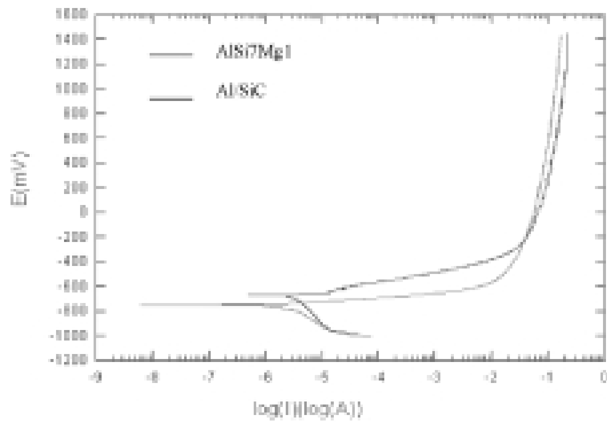

Figure 4: Curves of anode potentio-dynamic polarization for the extruded Al/SiC MMC and the AlSi7Mg1 alloy in 3.5% water solution of NaCl
Slika 4: Anodna potenciodinamična polarizacija ekstrudiranega kompozita Al/SiC in ekstrudirane zlitine AlSi7Mg1 v 3,5% vodni raztopini NaCl

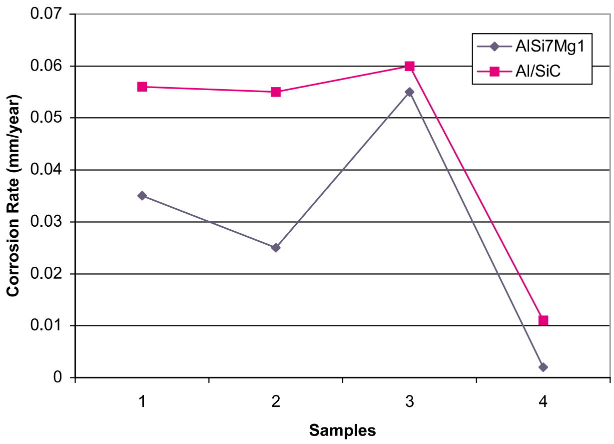

Figure 5: The comparison of corrosion rates for the Al/SiC composite and the AlSi7Mg1 alloy: **1)** as-extruded alloy in distilled water, **2)** heat-treated alloy in distilled water, **3)** as-extruded alloy in 3.5% water solution of NaCl, **4)** heat-treated alloy in 3.5% water solution of NaCl
Slika 5: Primerjava korozijskih hitrosti Al/SiC in AlSi7Mg1: **1)** zlitina v ekstrudiranem stanju, preizkušena v destilirani vodi, **2)** toplotno obdelana zlitina, preizkušena v destilirani vodi, **3)** zlitina v ekstrudiranem stanju, preizkušena v 3,5 % NaCl, **2)** toplotno obdelana zlitina, preizkušena v 3,5 % NaCl

3.2 Investigations of stress corrosion cracking

The investigations of SCC were performed with static loading of the test samples. The samples for these investigations have a standard size (10 mm in diameter) and the loading was fixed at 67% of the materials' yield strength. The selected corrosive medium was a 3.5% water solution of NaCl at room temperature (approximately 22 °C). This is the most commonly used medium for determining the SCC resistance of Al alloys. The anode polarization of the samples was performed at a current density of 3.7 mA/cm^2 for 72 hours. The samples were fractured in a standard tensile machine after intensive polarization in the pre-loaded condition. In this way, changes in the materials' strength due to attack by the corrosive medium were determined. The effect of SCC or its combined effect with hydrogen embrittlement can be reliably evaluated by the ductility change of the material. As a result, the change in the samples area was measured. The results are given in **Table 3**.

Table 3: Reduction in the area of selected materials in initial and corroded conditions
Tabela 3: Kontrakcija zlitin 'Z' za osnovno in korodirano stanje

Material	Z (initial) (%)	Z (corroded) (%)	ΔZ (decrease) (%)
AlSi7Mg1 (as extruded)	51	48	5
AlSi7Mg1 (heat treated)	39	38	3
Al/SiC (as extruded)	17	11	35
Al/SiC (heat treated)	8	7	12.5

On the basis of the SCC investigations and the results given in **Tables 3** and **4** the following conclusions are proposed:

- In spite of the high pre-loading of the samples in the chlorine medium, stress-corrosion cracking was not observed.
- On the basis of the electrochemical investigations in 3.5% NaCl (intensive corrosion of both materials), it can be concluded that the basic conditions for SCC, e.g. active crack tip and passive crack laterals, were not fulfilled. These conditions are established only in the potential region characteristic for the passive state of the alloy in the corrosive medium.
- The SCC investigations were performed under standard conditions, assuming that if the conditions for SCC are fulfilled then deep and branched cracks must be formed for the given polarization conditions. Metallographic investigations of the samples after the SCC experiments did not show the formation of such kinds of cracks.

Table 4: Area reduction of selected materials due to general corrosion
Tabela 4: Zmanjšanje premera 'D' vzorca zaradi delovanja splošne korozije

Material	D (initial) (mm)	D (corroded) (mm)	ΔD (decrease) (%)
AlSi7Mg1 (as extruded)	10	9.3	7
AlSi7Mg1 (heat treated)	10	9.5	5
Al/SiC (as extruded)	10	8.7	13
Al/SiC (heat treated)	10	9.0	10

During the experiments, the general corrosion of the AlSi7Mg1 and the Al/SiC composite was detected, this

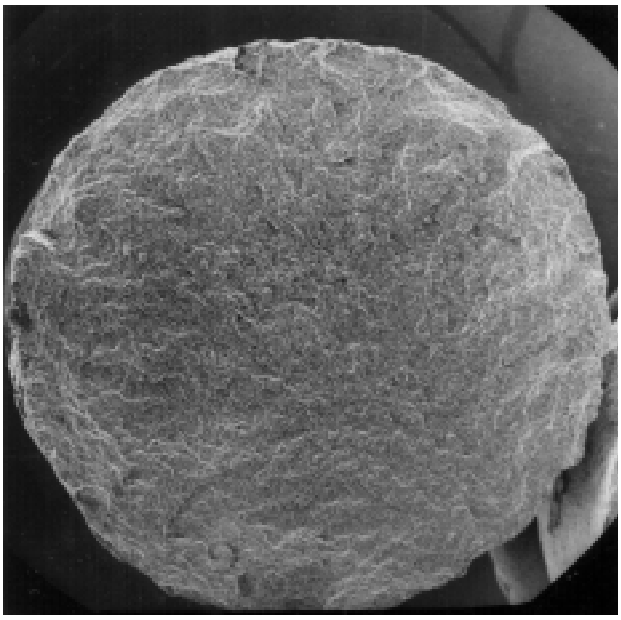

Figure 6: General corrosion in outer zone, AlSi7Mg1 alloy, mag.: 10 x
Slika 6: Zlitina AlSi7Mg1, 10-kratna povečava. Splošna korozija v zunanji coni

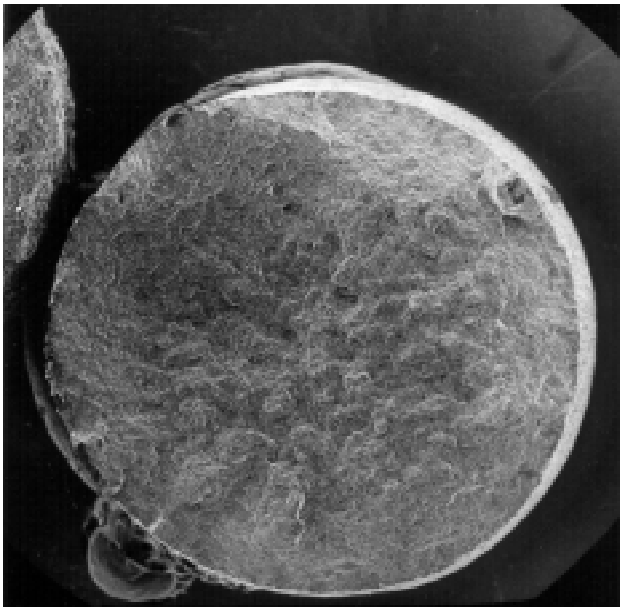

Figure 7: General corrosion in outer zone, Al/SiC composite, mag.: 10 x
Slika 7: Kompozit Al/SiC, 10-kratna povečava. Splošna korozija v zunanji coni

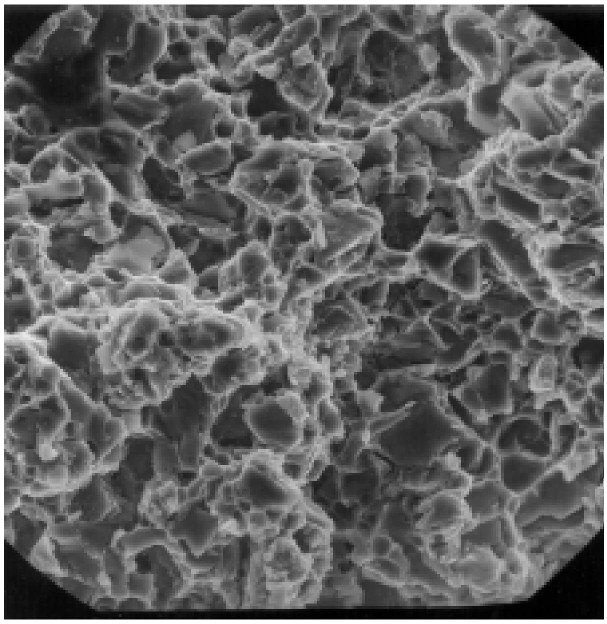

Figure 9: Edge of sample, Al/SiC compo-site, magnification: 500 x
Slika 9: Rob vzorca, kompozit Al/SiC, povečava: 500-krat

is reflected in the significant area reduction of the samples (**Table 4**). The area reduction for both materials is in accordance with the results of the electrochemical corrosion investigations of the alloys. SEM fractography carried out on both materials showed the absence of any SCC. In the surface zone of the AlSi7Mg1 alloy (**Figure 6**) and the Al/SiC composite (**Figure 7**) stress-corrosion damage was not observed. From the edge to the sample interior, traces of cracks were not found. The fracture surfaces exhibit a ductile fracture with a lower fracture energy (**Figures 8** and **9**). No inter- and intra-crystalline cracks were found on the fracture surfaces. The ductile de-cohesion shows that SCC did not occur.

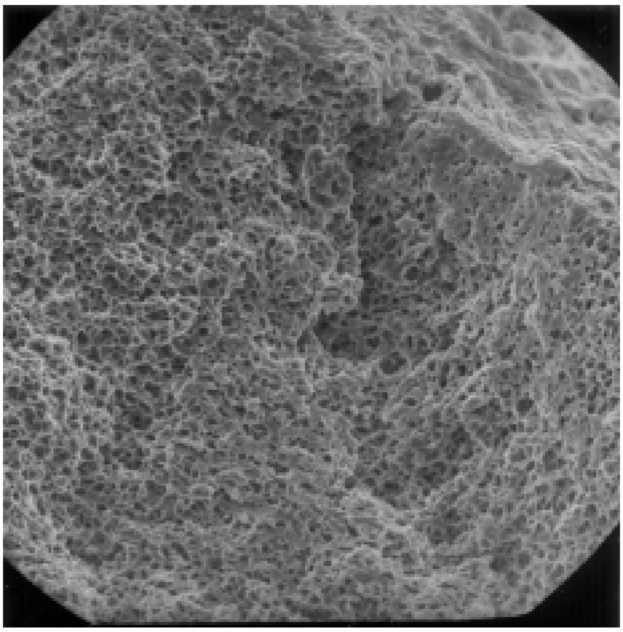

Figure 8: Edge of sample, AlSi7Mg1 alloy, magnification: 200 x
Slika 8: Rob vzorca, zlitina AlSi7Mg1, povečava: 200-krat

The determination of the area of the sample after SCC testing is very important, since it reliably defines the brittleness of the sample exposed to stress corrosion. Stress-corrosion cracks cause strong de-cohesion and a large decrease in the effective bearing cross-section. All these are characteristics of the extended branched stress corrosion which propagates into the bulk material causing a significant reduction in the area of the tensile test specimens. However, our investigations show that samples exposed to stress corrosion have a little corrosion damage only in the surface layer (**Figures 6** and **7**). This damage is characteristic for surface corrosion and not for stress corrosion. The ductility of SCC-tested samples is lower in comparison with the ductility of samples in the initial condition. The decrease in the area reduction is not a consequence of the stress corrosion but of hydrogen embrittlement. In other words, microstructural defects act as a trap for atomic hydrogen which significantly increases the brittleness of the material in the neighborhood of the microstructural defects.

4 CONCLUSIONS

From the corrosion investigations performed on the AlSi7Mg1 alloy and the Al/SiC composite it can be concluded that:

- Both alloys, independent of their condition (extruded or heat treated), do not form a passivation layer in both the chosen corrosion media. However, the corrosion rate is very low and amounts only to some hundredths or thousandths of a millimeter per year. The corrosion rate in the chlorine medium is greater, however, it is also relatively small. Therefore, it can be concluded that both selected materials exhibit good corrosion resistance.

- SCC investigations clearly showed that both materials are resistant to this type of corrosion, which occurs in high-strength Al-alloys.
- Only shallow surface corrosion was observed.
- The reduced ductility of pre-stressed Al/SiC specimens results from the activity of atomic hydrogen. Hydrogen accumulates at various defects and inclusions in the composite material. The investigated composite material contains a fine dispersion of SiC particles and therefore logically the number of such critical places is increased and the ductility of the material decreased.

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