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PROPERTIES OF AlSi5Cu1Mg MODIFIED WITH Sb, Sr AND Na

LASTNOSTI ZLITINE AlSi5Cu1Mg PO MODIFIKACIJI S Sb, Sr IN Na

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The properties of the secondary AlSi5Cu1Mg alloy, modified with Sb, Sr or Na, used as a cast housing for the automotive industry were investigated. The alloy was prepared from secondary aluminium and the properties of the material from the castings were determined. Presented here are the results of the mechanical tests of the as-cast and heat-treated material (T6), metallographic investigations and EDS analyses of the intermetallic phases based on Fe as well as electrochemical corrosion tests in a solution of 3 % NaCl. In the microstructure and with respect to the corrosion resistance of the alloys, modified with Sb, Sr or Na, no important differences were observed. The tests confirmed that the mechanical properties of cast-on bars from secondary aluminium AlSi5Cu1Mg were suitable for the application, only the microporosity of the castings needs to be eliminated through the selection of the proper casting parameters.

Keywords: secondary aluminium, modifiers, AlSi5Cu1Mg, mechanical properties, intermetallic phases, EDS analysis, microporosity, corrosion resistance

Opravljene so bile aktivnosti za uporabo sekundarne aluminijeve zlitine AlSi5Cu1Mg, modificirane s Sb, Sr ali Na, za lita ohišja za avtomobilsko industrijo. Zlitina, izdelana iz sekundarnega aluminija, je bila preizkušena in določene so bile lastnosti materiala, vzetega iz stene ulitkov. Predstavljeni so rezultati mehanskih preizkusov materiala v litem in v toplotno obdelanem stanju (T6), rezultati metalografskih preiskav in EDS-analize intermetalne faze na osnovi Fe, kot tudi elektrokemijski korozijski preizkusi v 3-odstotni raztopini NaCl. Niso bile ugotovljene pomembne razlike pri vplivu modifikatorjev Sb, Sr ali Na na mikrostrukturo in korozijsko odpornost zlitin. Preizkusi so potrdili, da so mehanske lastnosti prilitih palic iz sekundarne aluminijeve zlitine AlSi5Cu1Mg primerne za uporabo, potrebna pa je odprava mikroporoznosti ulitkov z izbiro primernih parametrov pri litju.

Ključne besede: sekundarni aluminij, modifikatorji, AlSi5Cu1Mg, mehanske lastnosti, intermetalne faze, EDS-analiza, mikroporoznost, korozijska odpornost

1 INTRODUCTION

The availability of primary and secondary raw materials and energy are of great concern in the metallurgical industry and in the other base-materials industries.[1] Less than a quarter of the current aluminium demand is covered by scrap from used products. However, the recycled content of aluminium products is not low because of inefficient recycling, but because of increasing demand for long-life products.[1] This recycling will also increase in the future with more sophisticated recycling methods.[2]

Remelting aluminium requires about 5–10 % of the energy required for primary production, so that recycling is very attractive from an energy point of view.[3] To produce primary aluminium the largest amount of electricity is required for electrolysis, while for the mining, transport and production of alumina and anodes only minor amounts of energy have to be supplied.

In the process of melting aluminium scrap, about 12 % of the metal is burnt and about 10 % of it is lost because aluminium mixes with the slag removed from the surface of the molten metal.[4–6]

The recycling of aluminium alloys[7–9] is also important from the environmental point of view.

The quality of secondary aluminium mostly depends on its residual Fe content and the formation of intermetallic phases based on Fe and other trace elements. Iron is a common impurity element in secondary aluminium alloys. In Al–Si foundry alloys, iron forms intermetallic compounds that are detrimental to the mechanical properties.[10]

It has been proven that the modification of eutectic silicon plays an important role in improving the mechanical properties of hypoeutectic Al-Si alloys. Elements that produce a refined, flake-like structure are antimony (Sb), arsenic (As) and selenium (Se). Only Sb, Sr and Na produce a significant modification at low levels of addition.[11]

The aim of the presented research was to evaluate the applicability of a secondary AlSi5Cu1Mg alloy, modified with Sb, Sr or Na, for the casting of housings from the point of view of microstructure, mechanical properties and corrosion resistance.

2 EXPERIMENTAL PROCEDURE

The melt of AlSi5Cu1Mg was prepared in a melting furnace from a mixture of secondary aluminium alloy ingots. The melt was alloyed with the necessary elements, degassed, modified with a Sb, Sr or Na modifier and cast. The required composition of the test alloys is presented in **Table 1**.

Table 1: Demanded range of elements in AlSi5Cu1Mg alloy, including modifier (mass fractions, *w*/%)

Tabela 1. Zahtevana okvirna sestava zlitine AlSi5Cu1Mg, vključno z modifikatorjem (masni deleži, *w*/%)

Element	Min. *w*/%	Max. *w*/%
Si	4.5	5.5
Cu	1.0	1.5
Mn		≤ 0.1
Mg	0.4	0.6
Zn		≤ 0.1
Ti		≤ 0.2
Fe		≤ 0.20
Ni		≤ 0.2
Individual impurity		≤ 0.05
Impurities Total		≤ 0.15
Modifier Sb	0.10	0.20
Modifier Sr	0.015	0.030
Modifier Na	0.0060	

The charge consists of a combination of ingots with close to the demanded chemical composition. The melt was prepared in a KEMOTERM melting furnace 600 kg. The melt was, prior to casting, degassed with argon for about 9 min. During the degassing the AlTi5B1 was added. The modifier in the form of AlSb10, AlSr10 or Na in the form of pills (Simodal 77) was added before the casting. The temperature of the melt during casting was 730 °C.

The castings were gravity cast into iron or sand forms. At the same time, cast-on bars were cast for comparison with tensile tests. After cooling the casting system was removed and from the wall of the castings the samples for the tensile tests were cut. The samples were treated using the T6 procedure: solution annealing: (527 ± 6) °C, 8 h, water cooling and artificial aging: (154 ± 5) °C, 8 h, cooling in air. For the tensile tests, as-cast samples were prepared as well as samples treated with the T6 procedure. The tensile tests were performed on an Instron 8802, tensile-testing machine 250 kN. The contact extensometer, mounted on samples, measured the stress-strain during the tensile tests.

The samples for the metallography were taken from both the thinner and thicker walls of the castings (**Figures 1a** and **1b**). The samples for metallography were prepared by a standard procedure. The intermetallic phases rich in Fe were observed with a light microscope (Microphot FXA, Nikon) using a 3CCD video camera (Hitachi HV-C20A) and computer software for the analysis. The intermetallic phases were also observed by scanning electron microscopy (JSM-6500F) with a field-emission source of electrons, INCA ENERGY Oxford Instruments, and analysed by energy-dispersive spectroscopy (EDS). The electrochemical corrosion tests of the material modified with Sb, Sr or Na were

Table 2: Chemical composition of tested alloys, modified with Sb, Sr or Na and cast into sand form and cast into an iron mould (mass fractions, *w*/%)

Tabela 2: Kemijska sestava preizkusnih zlitin, modificiranih s Sb, Sr ali Na in ulitih v peščeno formo ali v železno kokilo (masni deleži, *w*/%)

Element	Cast in sand form			Cast in iron mould		
Sample and modifier	59 – Sb	44 – Sr	62 – Na	237 – Sb	147 – Sr	333 – Na
Si	5.06	5.10	5.29	5.05	5.21	5.20
Fe	**0.1394**	**0.1528**	**0.145**	**0.151**	**0.153**	**0.1611**
Cu	1.326	1.622	1.40	1.188	1.112	1.376
Mn	0.0643	0.0541	0.0471	0.0378	0.0274	0.0562
Mg	0.4901	0.508	0.481	0.519	0.4438	0.527
Zn	0.0601	0.0662	0.0575	0.0489	0.0375	0.0658
Ni	0.0865	0.1761	0.107	0.0233	0.0071	0.0159
Cr	0.0036	0.0041	0.0033	0.0023	0.0020	0.0029
Pb	0.0020	0.0029	0.0022	0.0020	0.0012	0.0038
Sn	< 0.0010	< 0.0010	< 0.0010	< 0.0010	< 0.0010	< 0.0010
Ti	0.1015	0.171	0.110	0.0870	0.0935	0.1137
Be	< 0.0005	< 0.0005	< 0.0005	< 0.0005	< 0.0005	< 0.0005
Bi	< 0.0010	< 0.0010	< 0.0010	< 0.0010	< 0.0010	< 0.0010
Ca	< 0.0010	< 0.0010	< 0.0010	< 0.0010	< 0.0010	0.0010
Na	0.0015	0.0014	**0.0091**	< 0.0010	< 0.0010	**0.0089**
P	< 0.0010	< 0.0010	< 0.0010	< 0.0010	< 0.0010	< 0.0010
Sb	**0.0729**	0.0011	0.0037	**0.0984**	< 0.0010	< 0.0010
Sr	0.0017	**0.0195**	0.0020	0.0007	**0.0173**	0.0023
Zr	0.0050	0.0050	0.0109	< 0.0050	< 0.0050	< 0.0050
Co	< 0.0010	< 0.0010	0.0012	< 0.0010	< 0.0010	< 0.0010
Al	92.6	92.1	92.3	92.8	92.9	92.5

performed in a 3 % solution of NaCl. The test specimens were cut into discs of 15 mm diameter. The specimens were ground with SiC emery paper down to 4000 grit and rinsed with distilled water, prior to the electrochemical studies. The specimens were then embedded in a Teflon holder and employed as the working electrode. The reference electrode was a saturated calomel electrode (SCE, 0.242 V vs. SHE) and the counter electrode was a flat platinum mesh. All the potentials described in the text are relative to the SCE, unless stated otherwise.

The potentiodynamic measurements were recorded using a BioLogic SP-300 Modular Research Grade Potentiostat/Galvanostat/FRA and EC-LAB software 10.37 computer programs. In the case of the potentiodynamic measurements the specimens were immersed in the solution 1 h prior to the measurement in order to stabilize the surface at the OCP. The potentiodynamic curves were recorded, starting at 250 mV (SCE) more negative than the OCP. The potential was then increased, using a scan rate of 1 mV/s, until the transpassive region was reached.

3 RESULTS AND DISCUSSION

The chemical compositions of the tested alloys, cast in sand or cast in an iron mould, are presented in **Table 2**.

From **Table 2** it is evident that the content of the main impurity, i.e., iron, in the tested alloys is in the range of w = 0.13 % to w = 0.16 %. Presented here are also the contents of the elements for the modification of the alloys (Sb, Sr and Na).

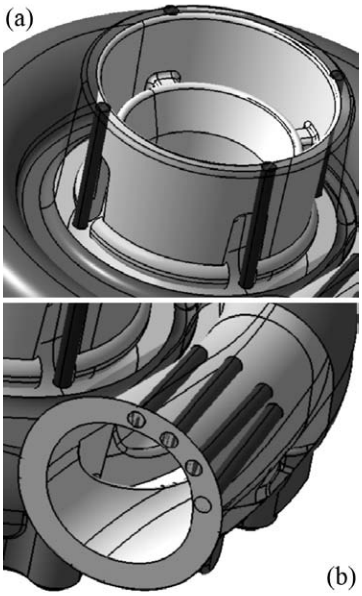

Figure 1: Schematic presentation of the location of the specimens Φ = (4 ± 0.05) mm, L_0 = (20.00 ± 0.04) mm, L_c = 55.0 mm for tensile tests (ASTM B 557 M-07): a) thinner wall, b) thicker wall

Slika 1: Shematski prikaz položaja vzorcev Φ = (4 ± 0,05) mm, L_0 = (20,00 ± 0,04) mm, L_c = 55,0 mm za natezni preizkus (ASTM B 557 M-07): a) tanka stena, b) debela stena

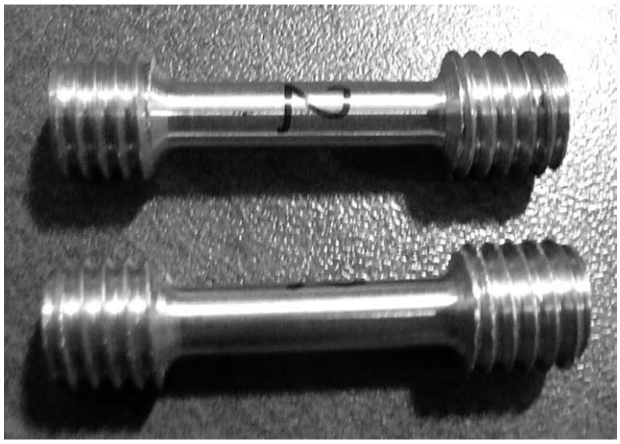

Figure 2: Tensile-test samples

Slika 2: Preizkušanca za natezni preizkus

The demanded mechanical properties for this type of AlSi5Cu1Mg alloy are presented in **Table 3**.

Table 3: Demanded mechanical properties of AlSi5Cu1Mg alloy, heat treated T6

Tabela 3: Zahtevane mehanske lastnosti zlitine AlSi5Cu1Mg, toplotno obdelane (T6)

$R_{p0.2}$	R_m	HB
> 185 MPa	> 285 MPa	80–90

Tensile test specimens were cut from the thin and thick walls of the housing, as schematically presented in **Figures 1a** and **1b**, heat-treated T6 and tensile tests were made (**Figures 2** and **3**). The results of the tensile tests of the samples cast in the mould and cast in the sand form and heat treated T6 are collected in **Tables 4** and **5**.

For comparison, the tensile test samples were also prepared from the bars of diameter 18 mm, cast in the iron mould. The tensile-test samples were machined and heat treated T6. The results of the tensile tests are presented in **Table 6**.

From **Tables 4** and **5** it is evident that the tensile properties $R_{p0.2}$ and R_m of the samples taken from the wall of the casting are below the demanded values. Better

Figure 3: Extensometer Instron, installed on tensile-test sample

Slika 3: Ekstenzometer Instron, nameščen na trgalnem preizkušancu mechanical properties are shown by the tensile samples prepared from the cast on bars.

Table 4: Mechanical properties of T6 heat-treated samples from housing, cast in sand form, thicker wall

Tabela 4: Mehanske lastnosti po toplotni obdelavi T6 vzorcev iz ohišja, ulitega v pesek, debela stena

Sample	$R_{p0.2}$/MPa	R_m/MPa	A/%	Z/%
59/1 Sb	170	186	1.5	4
59/2 Sb	159	191	1.8	3
59/3 Sb	163	201	2.6	3
44/1 Sr	173	216	2.0	5
44/2 Sr	169	197	1.6	3
44/3 Sr	168	174	1.6	3
62/1 Na	158	187	2.8	4
62/2 Na	161	176	2.6	4
62/3 Na	186	192	2.2	4
Mean value	**167**	**191**	**2.1**	**3.6**

Table 5: Mechanical properties of T6 heat-treated samples from housing, cast in iron mould, thicker wall

Tabela 5: Mehanske lastnosti po toplotni obdelavi T6 vzorcev iz ohišja turbo kompresorja, ulitega v kokilo, debela stena

Sample	$R_{p0.2}$/MPa	R_m/MPa	A/%	Z/%
237/1Sb	178	260	4.5	8
237/2Sb	203	246	3.0	6
237/3Sb	183	266	5.3	8
147/1Sr	172	247	6.1	9
147/2Sr	187	242	5.6	7
147/3Sr	174	253	5.8	9
333/1Na	180	211	3.2	4
333/2Na	189	234	4.2	5
333/3Na	155	228	3.1	6
Mean value	**180**	**243**	**4.5**	**6.8**

Table 6: Mechanical properties of cast-on bars, diameter 18 mm, heat-treated T6, cast in iron mould

Tabela 6: Mehanske lastnosti prilitih palic premera 18 mm po toplotni obdelavi T6, ulito v kokilo

Sample	$R_{p0.2}$/MPa	R_m/MPa	A/%	Z/%
1/1 – Sr	285	354	3.9	7
1/2 – Sr	273	337	3.1	5
1/3 – Sr	282	354	4.2	7
1/4 – Sr	278	351	4.6	8
2/1 – Sb	284	361	4.4	7
2/2 – Sb	287	356	4.0	6
2/3 – Sb	285	364	5.1	7
2/4 – Sb	284	352	3.8	6
3/1 – Na	279	365	6.1	7
3/2 – Na	288	333	2.0	4
3/3 – Na	285	327	1.4	4
3/4 – Na	291	356	3.5	5
Mean value	**283**	**351**	**3.8**	**6.1**

A comparison of the data from **Tables 4**, **5** and **6** reveals the difference in the mechanical properties of the castings and the cast-on bars. The main reason for the lower values of the samples from the castings was revealed by the metallography (**Figures 4** and **5**). Shrinkage

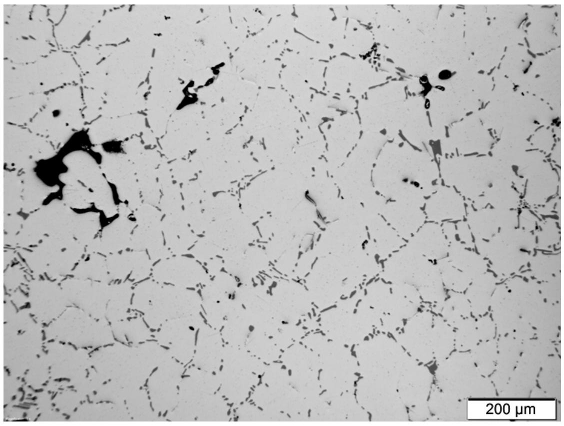

Figure 4: Shrinkage porosity in housing, thinner wall. The alloy was modified with Na.

Slika 4: Krčilna poroznost ohišja, tanka stena. Zlitina je bila modificirana z Na.

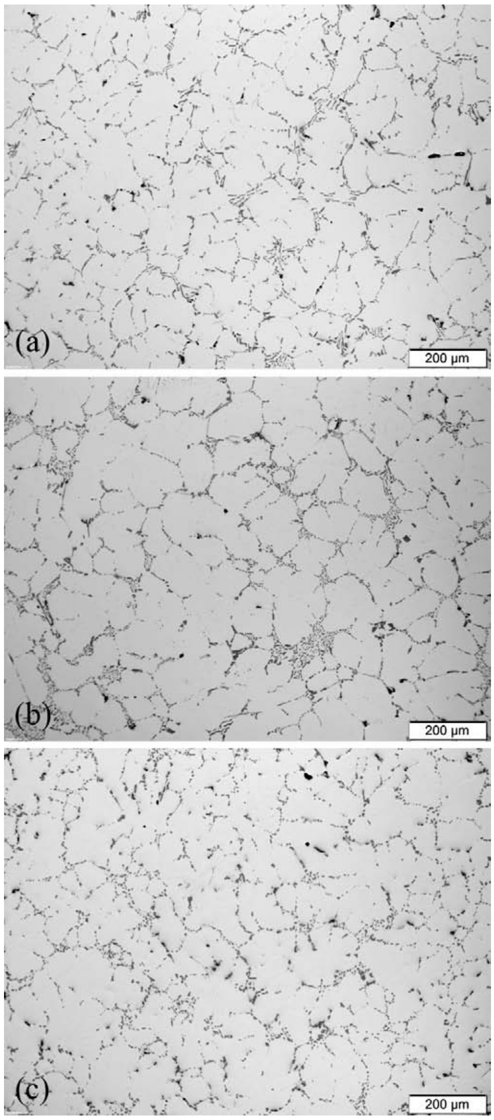

Figure 5: Microstructure of the cast on bars, after T6. Alloy, modified with: a) Sb, b) Sr and c) Na.

Slika 5: Mikrostruktura prilitih palic po T6. Zlitina, modificirana s: a) Sb, b) Sr in c) Na.

porosity was observed only in the castings. A similar porosity was observed at all three alloys, modified with Sb, Sr or Na. The appearance of the shrinkage porosity should be prevented by applying the appropriate measures involving melt treatment, gating/risering design and the effective use of the principles of directional and layered feeding.[12]

Besides the shrinkage porosity, also the presence of a needle-like Fe-based intermetallic phase was observed (**Figure 6**). To reduce the formation of the Fe-based intermetallic phase it is necessary to keep the Fe content in the secondary aluminium alloy as low as possible.

The basic microstructure of the alloy modified with up to 0.098 % Sb, 0.0182 % Sr and 0.010 % Na is presented in **Figure 5**. The microstructure of all three alloys is very similar.

Fe-based intermetallic phase are present in **Figures 6** and **7**.

Besides the light microscopy, also EDS analyses were performed on the Fe-rich intermetallic phases, as the most detrimental for the mechanical properties of secondary alloys. The results of the EDS analyses are presented in **Tables 7** and **8**. The as-cast sample (**Figure 6**, **Table 7**) was compared with the heat-treated T6 sample (**Figure 7**, **Table 8**).

Table 7: EDS analyses of areas marked on **Figure 6** (mass fractions, *w*/%)

Tabela 7: EDS-analize področij, označenih na **sliki 6** (masni deleži, *w*/%)

Spectrum	Al	Si	Mn	Fe	Cu	Mg
1	61.13	14.13	2.62	17.90	2.78	1.44
2	39.65	49.92	1.21	9.22		
3	5.75	94.25				
4	97.37	1.06			1.57	

As follows from **Figure 6** and **Table 7**, the Fe-rich intermetallic phase is plate- or needle-like and contains up to 17.9 % Fe in some cases up to 24 % of Fe. The EDS analyses confirmed, besides Fe, also other elements, such as Al, Si, Mn, Cu and Mg are present in the Fe-rich intermetallic phase.

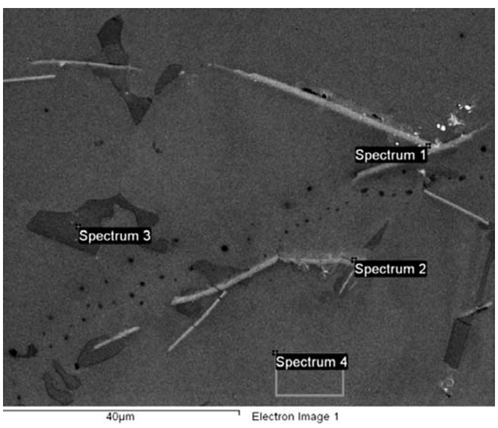

Figure 6: Fe-rich intermetallic, needle-like phase in the as-cast alloy modified with Sb. Marked are the positions of the EDS analyses.

Slika 6: Intermetalna faza, bogata z Fe, igličaste oblike v zlitini, modificirani s Sb. Označena so področja EDS-analiz.

Table 8: EDS analyses of areas marked on **Figure 7** (mass fractions, *w*/%)

Tabela 8: EDS-analize na mestih, označenih na **sliki 7** (masni deleži, *w*/%)

Spectrum	Al	Si	Mn	Fe	Cu	Ni
1	70.25	5.95		10.93		12.87
2	58.54	16.66	2.98	21.83		
3	83.20	8.59		8.22		
4	7.84	92.16				
5	61.57	9.67	2.43	21.02	3.33	1.98
6	58.20	16.46	3.27	22.07		
7	97.61	1.13			1.26	

Tables 7 and **8** present the EDS analyses of the different phases in the as-cast and heat-treated samples. Most of the Fe-rich intermetallics are plate like. The refinement of the intermetallic compounds that crystallize as the primary phase from the Al-Si-Fe alloy is possible by applying ultrasonic vibration at their nucleation temperature.[13]

In most cases the EDS analysis did not reveal the elements (Sb, Sr, Na) added for modification of the alloy. It looks as if the elements for modification are well distributed in the solid solution of the Al matrix and are not associated with the various phases in the microstructure of the alloy.

For the practical application of the alloys, the corrosion properties of the material are also important. As the most detrimental to the material is the influence of chloride ions, the electrochemical corrosion tests of alloys, modified with Sb, Sr or Na, were performed in a 3 % solution of NaCl. The results of the electrochemical corrosion test are presented in **Figure 8**. From the potentiodynamic measurements it can be concluded that the

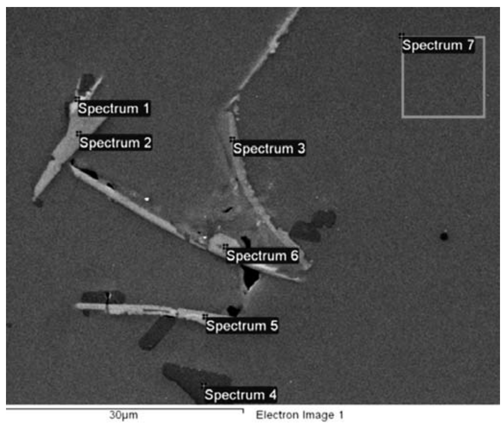

Figure 7: Fe-rich intermetallic, plate- and needle-like phase in T6 heat-treated alloy, modified with Sb. Marked are the positions of the EDS analyses.

Slika 7: Z Fe bogata intermetalna faza v obliki ploščic in igel v T6 toplotno obdelani zlitini, modificirani s Sb. Označena so področja EDS-analiz.

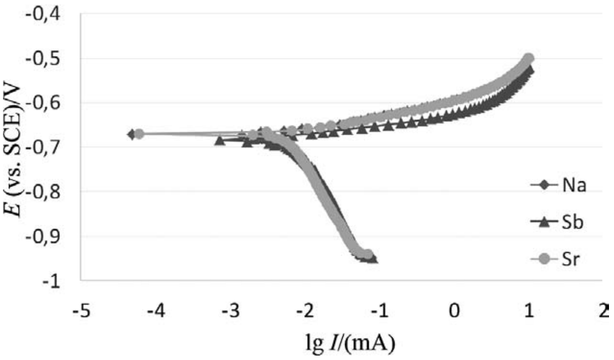

Figure 8: Potentiodynamic curves for AlSi5Cu1Mg alloys modified with Sb, Sr or Na in a solution of NaCl 3 %
Slika 8: Potenciodinamske krivulje za zlitino AlSi5Cu1Mg, modificirano s Sb, Sr ali Na v raztopini NaCl 3 %

corrosion properties in the Tafel area (± 250 mV around the Ecorr) do not show any significant differences between the studied materials. From the icorr and Ecorr we can conclude that no major difference exists in the corrosion resistance of the tested alloys of AlSi5Cu1Mg. The addition of a different modifier (Sb, Sr or Na) has no remarkable impact on the electrochemical corrosion behaviour of the AlSi5Cu1Mg alloy in a 3 % solution of NaCl.

4 CONCLUSIONS

Based on the investigation and a comparison of secondary AlSi5Cu1Mg alloys, modified with Sb, Sr or Na, the following conclusions can be drawn:

- A comparison of the microstructures of the AlSi5Cu1Mg alloys, modified with Sb, Sr or Na, did not reveal any noticeable differences.
- The microporosity was observed only in castings for all three modified alloys.
- The Fe-rich intermetallic phase is plate- and needle-like and contains up to w = 24 % of Fe.
- The poor mechanical properties of the castings in the as-cast or in the T6 state were a consequence of the shrinkage porosity.
- Higher values of $R_{p0.2}$ and R_m, as demanded, were only obtained for tensile tests of the cast-on bars after the T6 heat treatment. The reason is the absence of shrinkage porosity in the cast-on bars.
- The modification of the AlSi5Cu1Mg alloy with Sb, Sr or Na did not influence the corrosion resistance of the alloy in a 3 % solution of NaCl.
- The investigations confirmed the secondary alloy AlSi5Cu1Mg is conditionally suitable for the production of housings. The main concern is to hold the level of residual Fe as low as possible. The casting of housings should be made with proper process parameters (preparation of the melt, cast at proper temperature, suitable mould form), so as to eliminate the shrinkage porosity in the castings.

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