

Corrosion behaviour of the AlSi6Cu4 alloy and cast AlSi6Cu4-graphite particles composite

Z. Konopka^{a,*}, S. Holeczek^b, J. Pożar^b, M. Nadolski^a, M. Łągiewka^a, A. Zyska^a

^a Department of Foundry, Technical University of Częstochowa, ul. Armii Krajowej 19, 42-200 Częstochowa, Poland

^b Institute of Chemical Technology UKMKI, Technicka 5, 166 28 Prague, Czech Republic,

* Corresponding author's e-mail: konopka@mim.pcz.czyst.pl

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Abstract

The corrosion behaviour of the AlSi6Cu4 alloy as a composite matrix and of composites with 8% vol. of graphite particles was investigated. The corrosion experiments were performed over a range of elevated temperatures and were carried out in sea water (3.5% NaCl solution). We have focused our attention to the determination of the mode of corrosion attack and to the determination of the rate of corrosion and other corrosion characteristics. Both as-cast and annealed matrix and composite specimens were tested, as well as the 99.9% as-cast aluminium for comparison. Corrosion behaviour of the materials was assessed by the corrosion potential (E_c) and by potentiodynamic (polarization) curves. As expected, composite is less corrosion resistant than the matrix alloy. In addition to pitting, a severe galvanic corrosion occurs as a result of galvanic couple aluminium/graphite formation. Corrosion potentials imply that examined materials would be sufficiently resistant in non or slightly oxidizing solutions without dissolved oxygen. All studied materials corrode very slowly at potentials negative to corrosion potential, while at potentials positive to corrosion potential the corrosion rate goes up by 1 or 2 orders.

Keywords: corrosion, metal matrix composites, graphite particles

1. Introduction

Aluminium alloy matrix composites reinforced with different ceramic particles can be applied as a modern construction material in automotive industry, particularly for brake discs and pistons [1, 2, 3, 4]. However, the addition of the reinforcing particles can significantly influence the corrosion behaviour of these materials. Published literature concerning the corrosion behaviour of aluminium-based composites is rather limited and often contradicting in general. Different aluminium alloy matrices and different types of particle reinforcement and their combinations may exhibit a completely different corrosion behaviour. In addition, processing parameters of composites can affect microstructure and their corrosion properties [5, 6, 7, 8].

For example, studies on the 359/20%SiC composite corrosion resistance carried out by using the potentiodynamic method showed that the corrosion analysis of composite material was

related to the corrosion characteristics of AK9 (AlSi9Mg) aluminium alloy. These examinations did not show significant influence of SiC particles on the increase of the susceptibility to pitting corrosion in comparison to AK9 alloy, what is confirmed by the literature data [9,10].

Corrosion resistance of as-cast and heat treated AlZnMg-Al₂O₃ composite with 10 and 20% volume fraction of Al₂O₃ reinforcing particles was investigated in LiClO₄-H₂O solution. For specimens in the initial state quantity of corrosion pits was smaller than for heat treated composite [11].

Introduction of graphite particles into the AlSi matrix alloy decreased corrosion resistance of composite in comparison with the pure matrix alloy. Squeeze casting method used in composite technology generates beneficial changes of structure and increases corrosion resistance [12].

2. Methodics and the materials

The examined composites have been made of AlSi6Cu4 alloy matrix reinforced with 8 vol. % of natural graphite particles. This matrix alloy is commonly used in foundry technology and its composition assures good wettability and proper arrangement of graphite particles because of its wide solidification range. This way composite slurry can be easy achieved. The alloy exhibits good casting properties what enables production of castings with complex shape. Graphite particles of 70-100 μm size have been used for preparing the composites.

Composite suspension has been prepared by mechanical mixing method. The matrix alloy was melted in the induction crucible furnace and overheated up to the temperature of 993 K. Then reinforcing particles have been introduced into the stirred molten alloy by means of a dosing spout. Mixing has been done by turbine mixer of 0.05 m diameter equipped with four blades of the angle of slope equal to 45°, which have been placed at the distance equal to one-third of the height of the liquid metal from the bottom of crucible in its axis. The mixing time has been 10 minutes and the angular velocity of mixer has been set for 500 rpm. Composite production process parameters selected in this way have enabled the uniform distribution of graphite particles within the matrix volume.

After mixing the squeeze casting method was used for sample preparing. Slab-shaped specimen castings of dimensions 200×100×20 mm have been produced in the die block mounted on the PHM-250C hydraulic press. Pressing in a solid-liquid state has been realised at constant alloy temperature equal to about 923 K. The examination has been realised for the pressing pressure 90 MPa, and die temperature was 523 K.

The corrosion experiments were performed over a range of elevated temperatures and were carried out in sea water (3.5% NaCl solution). We have focused our attention to the determination of the mode of corrosion attack and to determination of the rate of corrosion and other corrosion characteristics. Both as-cast and annealed matrix (AK64) and composite (AM8) specimens were tested along with 99.9 % as-cast aluminium for comparison.

In order to reveal the mode of corrosion all diamond-polished specimens were immersed into the quiescent and atmospheric oxygen saturated solution for 24 hours. The specimens were then rinsed with distilled water, ethanol, dried and submitted to microscopic observation.

Quantitative corrosion measurements were performed in a laboratory three-electrode cell filled with 3.5% NaCl solution. Specimens were attached to a platinum wire that served as a working electrode, AgCl electrode was used as the reference one and counter electrode was made of platinum. The experiments were carried out in quiescent solutions. Fresh and oxygen saturated solution (30-60 minutes) was used for every experiment. Every specimen was measured at least three times and the potentials were related to AgCl reference electrode.

Corrosion behaviour of the materials can be assessed by the corrosion potential (E_c) and by potentiodynamic (polarization) curves. Corrosion potential was predicted using two ways: as a potential to be stuck at the metal/electrolyte interface in non current state and constant for at least 15 minutes and as a potential corresponding to zero current density in polarization

measurements. Potentiodynamic measurements were made at scanning rate of 60 mV/min and at the temperature of 298 K.

3. Results of the experiments

It was observed that the alloy and composite corrodes both in galvanic mode and by pitting in addition to crevice mode, whenever it is possible. Pitting is a dominant mode for the alloy and preferentially attacked phases are eutectic and the intermetallic compounds. Galvanic corrosion dominates in the corrosion of composite and results from aluminium solid solution/graphite cell formation and the vicinity of graphite particles is preferentially attacked.

Corrosion potential of as-cast 99.9 % aluminium was – 535 mV (vs. AgCl), while as-cast alloy and composite were more positive (-450mV and -525 mV respectively). Corrosion potential of both studied materials, however, shifted to more negative potentials (close to corrosion potential of pure aluminium) with increasing time of annealing. At the same time, large difference in corrosion potentials between matrix alloy and composite gradually ceased to very little values (less than 10 mV). Both of materials annealed at 400 °C were more positive than those annealed at 300 °C at annealing times longer than 20 hours. Corrosion potentials made very little alternations after annealing longer than 100 hours. All of these results are shown in Figure 1.

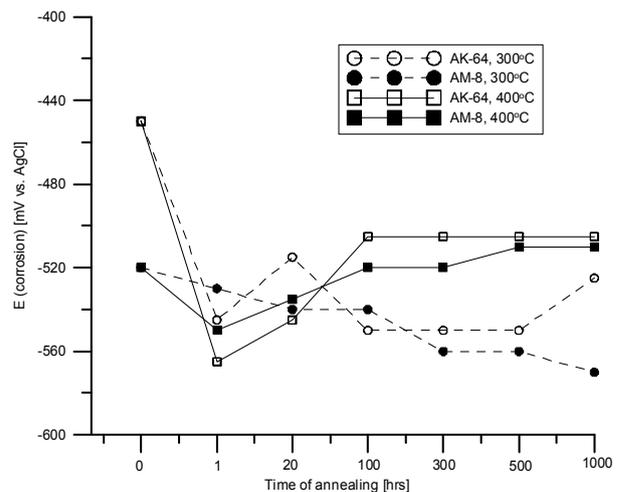


Fig.1. Time and temperature dependence of the corrosion potential of AISi6Cu4 alloy (AK64) and composite (AM8)

Figures 2a to 2c show results of polarization (potentiodynamic) measurements. They reveal the fact that none of the tested materials was able to passivate in 3.5% NaCl solution. Matrix alloy corrodes at a higher rate than 99.9% aluminium, but at a lower rate than composite. Corrosion behaviour of non-passivative materials is then dependent on the corrosion potential and the slope of polarization curve at positive (cathodic) current density: the more positive the corrosion potential and the lower the slope are, the more corrosion resistantly material behaves.

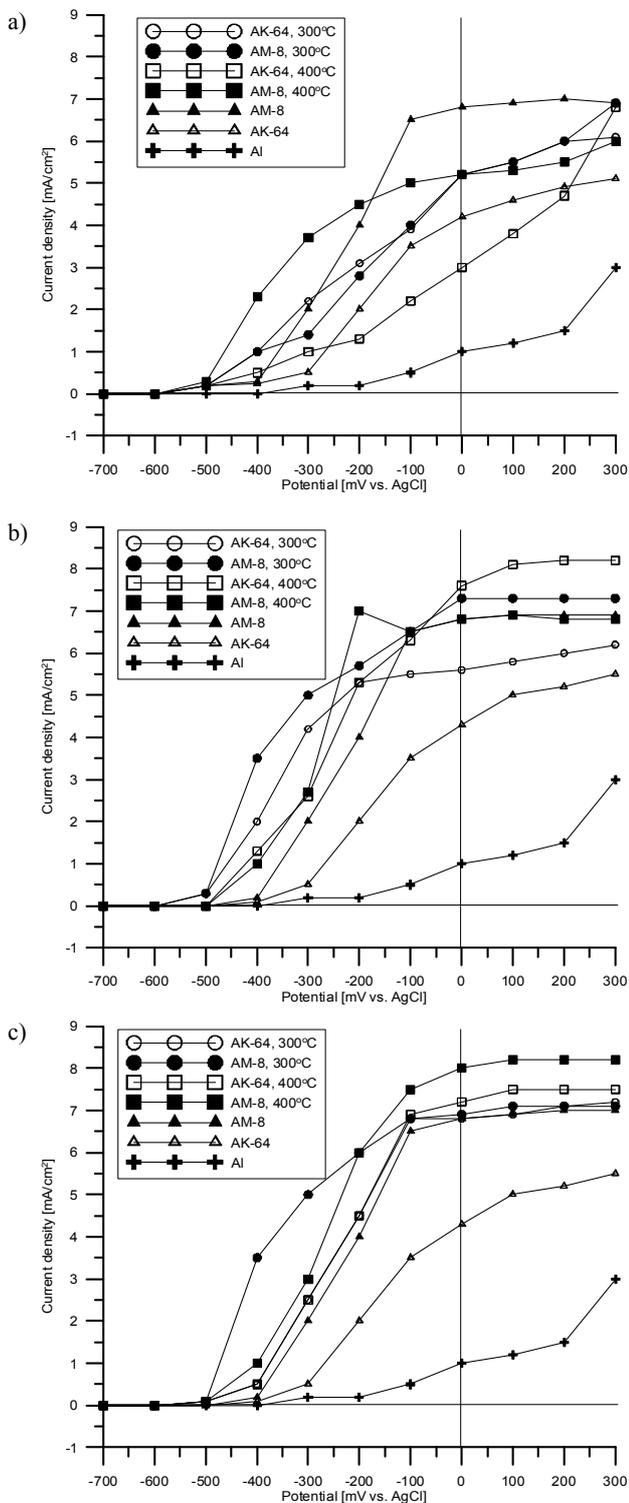


Fig 2. Potential - current density relationship of 99.9% as-cast aluminium, AlSi6Cu4 alloy (AK-64) and composite (AM-8) annealed at 573 K and 673 K for: a) 1 hour, b) 100 hours, c) 1000 hours

Our measured polarization curves have similar course: once corrosion potential is exceeded, the rate of corrosion (determined by the slope) accelerates until a steady state is reached. This trend is visible in the hyperbolic character of polarization curves.

As expected, composite is less corrosion resistant than matrix alloy. In addition to pitting, a severe galvanic corrosion occurs as a result of galvanic couple aluminium/graphite formation. Corrosion potentials imply that examined materials would be sufficiently resistant in non or slightly oxidizing solutions without dissolved oxygen.

It was found that annealing has very little, if any, effect on the corrosion behaviour of test materials in sea water. Thermally-treated materials corrode slightly faster than the as-cast ones. In a few cases, however, an opposite tendency was noticed.

4. Conclusions

Comparing the corrosion behaviour of all materials we may draw conclusion that:

- 1) As-cast matrix alloy corrodes in the same manner like as-cast composite, but at lower rate in the whole scale of potentials.
- 2a) One-hour annealing of matrix alloy at 300 °C slightly deteriorates its corrosion behaviour, while the same annealing at 400 °C makes a little improvement in corrosion behaviour (Figure 4a).
- 2b) 100 and 1000-hour annealing of matrix alloy increases its corrosion rate with increasing annealing temperature (Figures 4b and 4c)
- 3a) 1-hour annealing of the composite at 300 °C improves corrosion behaviour at all potentials, while the same procedure made at 400 °C has the same effect at potential above -200 mV (Figure 4a).
- 3b) 100 and 1000-hour annealing of composite result in decrease of corrosion behaviour up to -200 mV, at potentials more positive than this value the behaviour of annealed and as-cast composite is very similar (Figures 4b and 4c).
- 4a) Corrosion behaviour of the matrix and composite annealed at 300 °C for 1 hour is the same, while at 400 °C matrix corrodes distinctly more slowly than the same heat treated composite.
- 4b) Matrix corrodes almost at the same rate as composite in the whole scale of potentials after 100 and 1000 hour-annealing at 300 °C and 400 °C.
- 5) All studied materials corrode very slowly at potentials negative to corrosion potential, while at potentials positive to corrosion potential the corrosion rate goes up by 1 to 2 orders.
- 6) Aluminium corrodes at many times lower rate than both matrix alloy and composite.

At the end it is possible to state that both of examined materials resist more to elevated temperature than to aggressive corrosion environment. At elevated temperatures, however, drop in hardness (and likely in strength) takes place. The differences in corrosion resistance are rather caused by different composition than by heat history of material.

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