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INFLUENCE OF LASER SURFACE HARDENING ON CORROSION PROPERTIES OF Al-Zn-Si CAST ALLOY

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This work is focused on the effect of the laser surface treatment (laser power 50 and 80 W) on microstructure and corrosion properties of self-hardened AlZn10Si8Mg cast alloy used for engine and vehicle constructions. The electrochemical impedance spectroscopy (EIS) technique and Nyquist plots in a 1M NaCl test solution at 20 °C were carried out. A detailed corrosion study showed that corrosion resistance samples with laser layer were marginally less; probably the presence of chloride ions significantly damaged the Al_2O_3 film and caused the formation of $NaAlO_2$.

Key words: Al-Zn-Si cast alloys, laser surface hardening, microstructure, corrosion properties

INTRODUCTION

Advanced automotive applications require materials with special surface properties such as high corrosion and wear resistance and hardness. Alloys possessing these properties are usually very expensive and their utilization drastically increases the cost of the parts. On the other hand, failure or degradation of automotive components due to mechanical and chemical (electrochemical) interaction with the surrounding environment is most likely to initiate at the surface because the intensity of external stress and environmental attack are often highest at the surface [1-4].

Laser surface melting is a well established technology applied to many materials for hardening, reducing porosity and increasing wear and corrosion resistance. Modifications to the surface properties of the material are due to rapid melting followed by rapid solidification. The intimate contact between the melt and the solid substrate causes a very fast heat extraction during solidification, resulting in very high cooling rates of the order of 10^5 to 10^8 k/s [1, 5-6].

Materials processed via rapid solidification tend to show advantages of refined microstructure, reduced micro segregation, extensive solid solubility and formation of metastable phases. It is generally accepted that the improvement in corrosion performance is due to refinement (homogenisation) of microstructure and dissolution (redistribution) of precipitates or inclusions, which result from rapid solidification [5-7].

In recent years there has been interest in the use of laser technology for the realisation of corrosion resistant surfaces on engineering alloys based on steel. More recently, there has been a growing interest in improving the corrosion performance of aluminium alloys by laser techniques to those used for steel.

Recycled Al-Zn-Si casting alloys can often be used in new cast products for mechanical engineering, hydraulic castings, textile machinery parts, car components or big parts without heat treatment [8-10].

The present study is part of a larger research project, which was conducted to investigate and provide better under-standing of the properties of secondary Al- cast alloys.

This work focuses on the effect of the laser surface treatment on corrosion properties of AlZn10Si8Mg cast alloy.

EXPERIMENTAL

We used a secondary (scrap-based - recycled) unmodified AlZn10Si8Mg cast alloy with very good mechanical properties after casting, good casting properties, good wear resistance, low thermal expansion and very good machining [8]. The chemical analysis of the experimental cast alloy was carried out using an arc spark spectroscopy and the chemical composition is shown in Table 1.

Table 1 **Chemical composition of AlZn10Si8Mg cast alloy / wt. %**

Zn	Si	Fe	Mn	Mg	Ti	Al
9,60	8,64	0,12	0,18	0,45	0,06	bal.

This is a self-hardening alloy that is particularly used if good strength values are required without the need for heat treatment. Self-hardening starts when the castings are removed from the mould and the final mechanical properties are achieved after storage for approximately 7 to 10 days at room temperature. Test bars (ø 20 mm with a length of 300 mm) were produced by

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sand casting. The melt was not modified or grain refined. Bars were then machined to produce unnotched impact test specimens (10 x 10 x 55 mm).

Laser treatment (Nd: YAG type) with pulse power beam 50 and 80 W was applied on the cross-section area of the samples for bending impact toughness test.

After the laser treatment, the samples were sectioned and transferred to corrosion test and structural analysis. In order to evaluate the effects of laser surface hardening on the corrosion behaviour we used electrochemical impedance spectro-scopy (EIS) [11]. The electrochemical corrosion tests were performed in a 1 cm^2 circular area of ground sample surfaces (base material and laser treated materials). In the experiment, a sinusoidal voltage of 5 mV and a frequency range of 100 kHz to 10 mHz were used. Impedance measurements of the EIS experiment are displayed in the form of Nyquist plots as a function of immersion time up to a period from 5 min to 24 hour (temperature 20 °C ± 1 °C). The corrosion resistance of the specimens before and after laser surface melting was studied in 1 M NaCl solution.

Metallographic samples were prepared from selected specimens for bending impact toughness test (after testing) and the microstructures were examined by optical and scanning electron microscopy (SEM). As-cast and laser treated specimens were sectioned and prepared by standard metallographic procedures and etched by 0,5 % HF or Weck-Al. Some samples were also deep-etched in HCl solution in order to reveal the Si-morphology. Microhardness measurements HV 0.01 of sample surfaces affected by the laser with different pulse power were performed by a Zwick/Roell ZHm tester.

RESULTS AND DISCUSSION

The microstructure of experimental cast alloy (Figure 1a) consists of the primary phase (α-solid solution), eutectic (mixture of α-matrix and fine spherical Si-particles) and various types of intermetallic phases [12, 13]. The α-matrix precipitates from the liquid as the primary phase in the form of dendrites and is nominally comprised of Al and Zn.

The experimental material was not modified; therefore eutectic Si particles are like small grains - poorly rounded. Thickened grains were observed on the periphery of α-phase dendrites. After deep etching (Figure 1b) we can see that the Si is crystallized in the form of bars, which grow as a cluster from a single nucleating site. 3-D form bars correspond to metallographic sections, i.e. bunchy in the middle of the arrangement prevailing fine round bars and outwards; we can observe an increased incidence of the so-called plate type with a typical hexagonal shape, characteristic for non-modified alloys.

The laser beam action on the surface of the secondary alloy AlZn10Si8Mg has changed the microstructure (Figure 2).

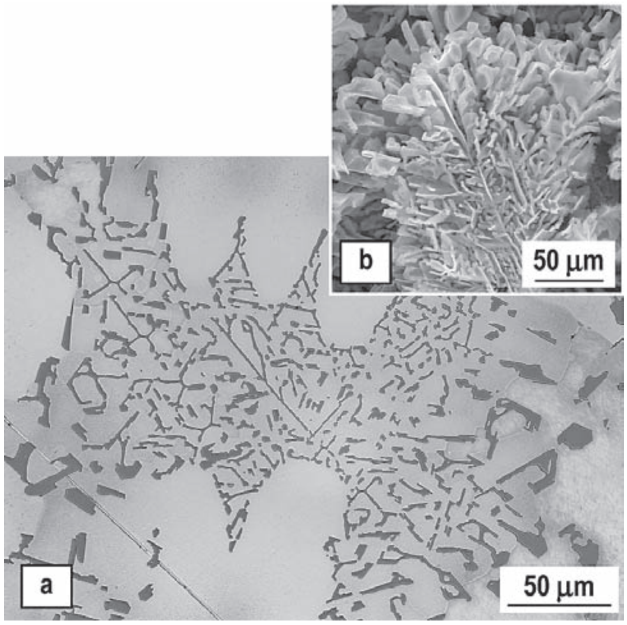

Figure 1 Microstructure of AlZn10Si8Mg cast alloy, as-cast state, etch. 0,5 % HF

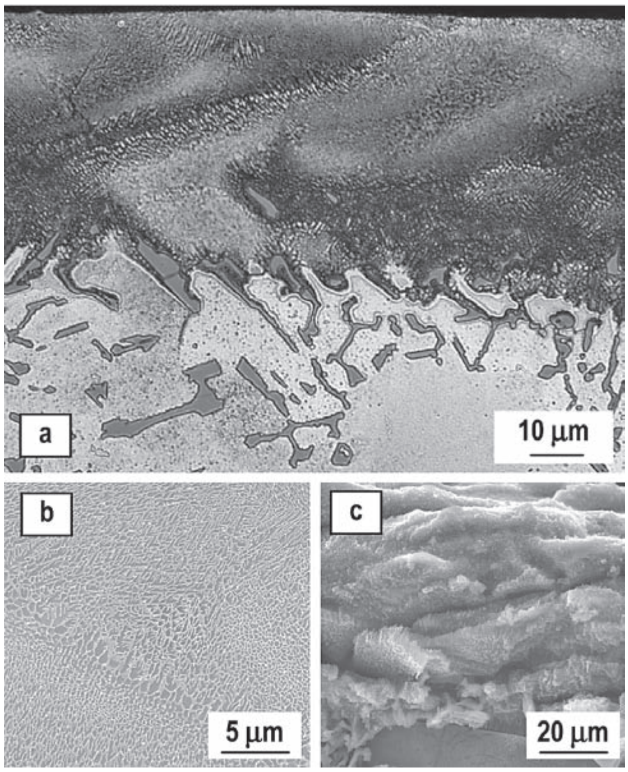

Figure 2 Microstructure of AlZn10Si8Mg cast alloy, laser layer, etch. Weck-Al

By laser remelting of the thin surface layer it is possible to achieve changes in the microstructure of the experimental alloy induced by high heating and cooling rates (Figure 2a). High cooling rates of the homogeneous melt give us an important effect of formation of fine columnar dendrite microstructure. Thus, formation of very fine and homogeneous microstructure of the solution crystals of silicon can be explained by thermo kinetic processes caused by high cooling rates (Figure 2b).

Figure 2a shows the remelted area and the transition of the remelted zone into the basic microstructure. In the transition area, grain refinement of eutectic Si (finer and rounder Si particles) as the modifying action of the laser was observed. The remelted area with columnar dendrite structure after deep etching is documented in Figure 2c.

With an increase in the laser power, the thickness of remelting zone increased (from approx. 47 μm after 50 W power to approx. 108 μm after 80 W). Microhardness of the surface layer increased from 94 HV 0.01 (as-cast state) to 140 HV 0.01 after the laser treatment.

Corrosion resistance is an important issue in aluminium alloys. There are several methods of surface engineering to improve the corrosion behaviour of aluminium alloys - each of them having advantages and disadvantages. Laser surface melting is one of those techniques. There have been a number of studies of the influence of laser melting on the corrosion properties of aluminium alloys, and the results achieved have been ambiguous with respect to the benefits of laser melting.

In some cases, it is severally accepted that laser surface melting can be used to improve the localized corrosion resistance of aluminium alloys as a result of homogenization and refinement of microstructures, and phase transformations.

The corrosion resistance of the experimental specimens before and after laser surface melting was studied in 1 M NaCl solution according ASTM International as a function of time up to a period from 5 min to 24 hour at temperature 20 °C ± 1 °C.

In this EIS technique, a small-amplitude sinusoidal potential perturbation is applied to the working electrode at a number of discrete frequencies. At each one of these frequencies, the resulting current waveform will exhibit a sinusoidal response that is out of phase with the applied potential signal by a certain amount. A standard calomel electrode was used as a reference electrode and platinum mesh was used as the counter electrode.

An appropriate model (EC-Lab V10.02) for equivalent circuit quantification was used as well. Impedance parameters such as polarization resistances (R_p) and capacitances (*CPE*) were obtained by using the equivalent circuit technique. The equivalent electrical circuit and impedance parameters are shown in Figure 3. Total polarization resistance of the specimen's surface is the sum of the partial polarization resistances R_{p1} and R_{p2}.

A detailed analysis of the corrosion data displayed in the form of Nyquist plots (Figures 4, 5) reveals that laser surface melting shows different corrosion behaviour. In general, the plots for all the as-cast and laser-treated specimens are similar: they consist of one capacitive loop.

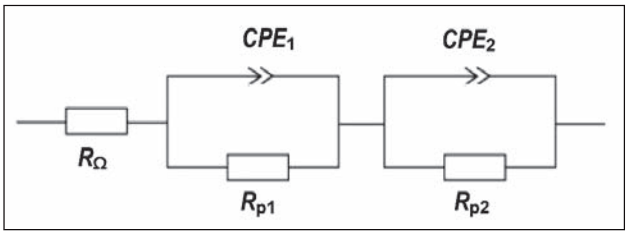

Figure 3 Equivalent electrical circuit for as-cast and laser hardened AlZn10Si8Mg alloy

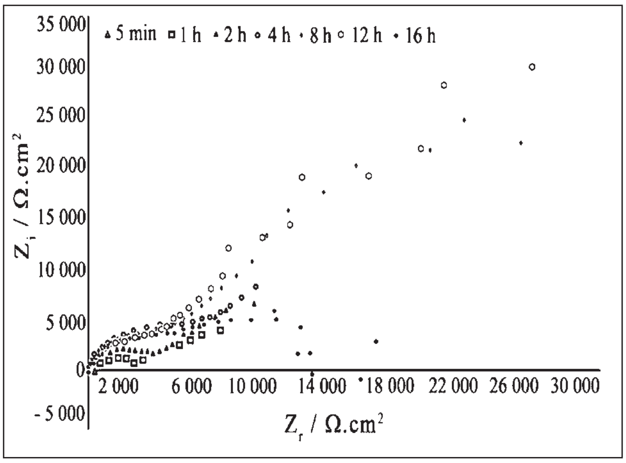

Figure 4 Nyquist plots for AlZn10Si8Mg alloy (as- cast state) in 1 M NaCl solution

For as-cast samples corrosion resistance decreased after 16 hours; maximal polarisation resistance was measured for 12 hours (38 973.4 Ω.cm^2).

In laser melted AlZn10Si8Mg cast alloy (with laser power 50 W) the maximal polarisation resistance was

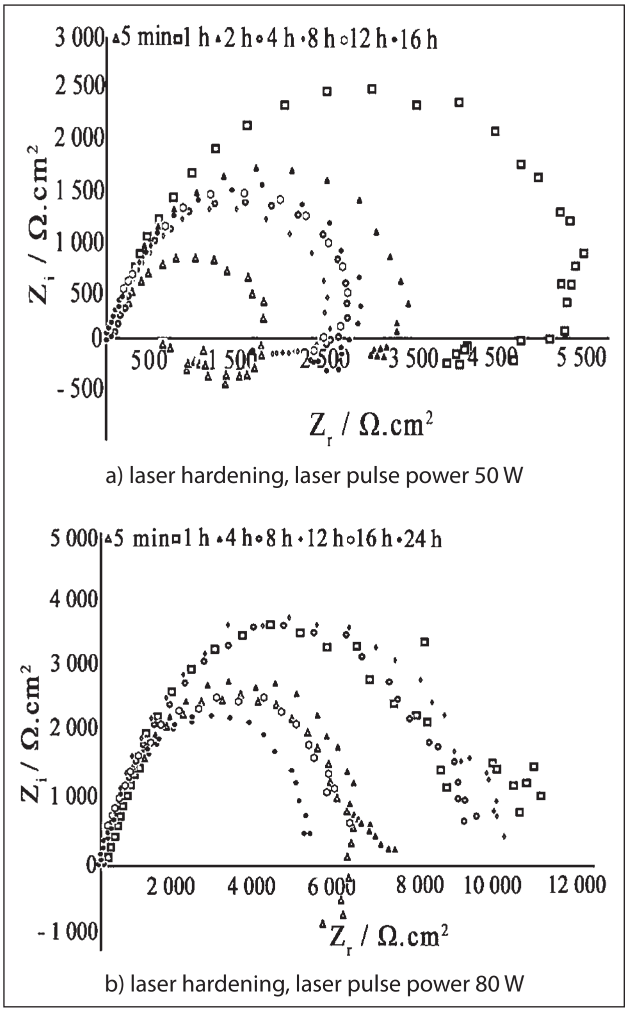

Figure 5 Nyquist plots for AlZn10Si8Mg samples in 1 M NaCl solution

measured up to 1 hour (5 620.5 Ω.cm^2); corrosion resistance decreased as soon as after 2 hours. Increasing the laser power to 80 W increased polarisation resistance after 5 minutes, which means that samples with a bigger remelted zone (108 μm) have better corrosion resistance than samples with a remelted zone of 47 μm. All polarisation values were measured above 5 000 Ω.cm^2 and maximal polarisation resistance was observed up to 1 hour (13 826.5 Ω.cm^2). For next exposure duration (8 - 12 hours) the resistance had settled at approx. 10 000 Ω. cm^2, but the coating stability is insufficient; whereupon after 16 hours corrosion resistance markedly decreased.

A detailed corrosion study showed that the use of laser surface remelting has provoked a deleterious effect on the corrosion behaviour of the AlZn10Si8Mg cast alloy. As-cast samples tend to have higher corrosion resistance than laser remelted samples. Corrosion resistance samples with laser layer were marginally less; probably the presence of chloride ions significantly damaged the aluminium oxide (Al_2O_3) film and caused the formation of $NaAlO_2$. The aluminium oxide film that formed on the specimen by oxidation in air did not provide an effective barrier against the adsorption of aggressive ions at the surface, and this led to active corrosion reactions.

CONCLUSIONS

In the present study, the effect of the laser surface treatment on corrosion properties of secondary AlZn10Si8Mg cast alloy was investigated. From the analysis of the results the following conclusions can be drawn:

- After solidification of the surface remelted layer a fine-grained microstructure was formed.
- With the given remelting conditions (50 or 80 W laser beam power) the depth of the remelted layer varied between 47 μm and 108 μm.
- The process of laser remelting caused improvement of microhardness in the remelted surface layer. High quantities of Si in the alloy that were additionally modified with other alloying elements causing the microhardness increase from 94 HV 0.1 in base alloy to 140 HV 0.1 in laser surface remelted layer. Such a microhardness increase of the remelted layer represents 48 % increase in microhardness regarding to the base alloy.
- A detailed corrosion study showed that corrosion resistance samples with a laser layer were marginally less; probably the presence of chloride ions significantly damaged the Al_2O_3 film and caused the formation of $NaAlO_2$.

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