CORROSION PROPERTIES OF SIC REINFORCED SURFACE LAYERS OF ALUMINIUM ALLOYS BY LASER BEAM MELT INJECTION

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ABSTRACT

Aluminium alloys are widely used due to their low density as well as high thermal and electrical conductivity. The disadvantage of low wear resistance can be overcome by different methods of surface modification. The use of high power lasers is a flexible tool in formation of wear protective layers on aluminium alloys. Laser melt injection of alloying and reinforcing powders allows formation of near surface layers with strongly improved wear resistance. Reinforcement of AlMgSi 1 (A 6082) and AlZnMgCu 1.5 (A 7075) is carried out by Nd:YAG cw laser with 2 kW maximum power using pure SiC and AlSi40-SiC powder mixtures. Microstructure of the produced layers is analyzed by optical and scanning electron microscopy (SEM). Corrosion behaviour is studied by immersion in 3.5% NaCl solution. Electrochemical characteristics are investigated by current density-polarisation curves. Also wear resistance of modified layers is proved by abrasive and adhesive wear tests.

KEY WORDS - corrosion resistance, aluminium alloys, laser melt injection, SiC reinforcement

INTRODUCTION

Laser surface treatment involves the application of short, high power laser pulses to melt the surface of a material, which then rapidly solidifies. The technique can be used for local surface treatment as well as for treatment of large surface areas. Possibilities of enhancing the corrosion performance of aluminium and its alloys by means of laser surface treatment techniques are widely investigated. Special attention is paid to local corrosion improvement. These techniques mainly include surface melting of pure material and laser surface alloying with different elements [1]. The effect on corrosion performance can be explained by microstructural modification together with the incorporation of non-equilibrium concentrations of alloying
elements resulting from rapid cooling rates compared with conventional surface treatment techniques, which provides the basis for property enhancement.

Published experimental data are often rather controversial. Some publications consider the improvement of pitting corrosion resistance of aluminium alloys due to dissolving of Cu containing precipitates in the remelted layers [1,2]. Other authors report that besides a slight improvement of corrosion resistance to general corrosion an improvement of pitting potential was not observed [3-5]. Surface melting of aluminium alloys modifies the structure of surface layers resulting in cells and/or cellular dendrites of very fine microstructure. For example for A2024-T3 alloy there are mainly two phases, i.e. primary solid solution and precipitated Al2Cu phase, around the cell boundaries. Some minor traces of Fe and Mn are also present. The estimated decrease of Cu content in precipitates is approximately 25%. The susceptibility to pitting corrosion of laser melted A2024-T3 surfaces characterised by pitting potential was not improved in comparison with as-received material, mainly due to non-uniform microstructure at transitions to subsequent laser tracks.

Use of excimer lasers for treatment of aluminium alloys is attractive due to high photon energy and better energetic coupling with materials. As an example of industrial application the corrosion resistance improvement of alloys was proposed applying scanning of large surfaces by irradiation by KrF and XeCl excimer lasers with the aim to improve pitting corrosion resistance of aluminium and steel [6]. It was shown that in the case of A2017, this improvement is due to the dissolution of khatyrkite phase (Al2Cu) in the matrix leading to a redistribution and content increase of the copper atoms within the aluminium solid solution.

Improvement of the intergranular corrosion resistance of the alloy 6013-T651 was also reached by excimer laser surface treatment of aluminium alloys under two different gas environments: air and nitrogen [7]. Excimer laser surface treatment significantly increased the pitting potential due to the reduction of large intermetallics within the grains. Authors show that besides this improvement the superior corrosion resistance of the N2 treated material is attributed to the presence of the chemically stable AlN phase in the surface.

The number of applications of aluminium alloys is also strongly reduced by the rather poor surface properties, especially wear resistance and hardness. Different ways exist to overcome this problem, such as deposition of different kinds of wear resistant coatings or formation a composite layers directly at the surface of the material. One of the methods is the laser melt injection process that is a technique to produce a metal-matrix composite (MMC) layer on top of a metal workpiece [8,9].

The aim of this work was to study the influence of inhomogeneities caused by laser dispersing of hard particles in near surface zones of aluminium alloys on their corrosion properties.

MATERIALS AND METHODS

During the applied laser dispersing process reinforcing particles are injected directly into the melt bath, which is formed by laser irradiation on the surface of the processed material. Variation of treatment process parameters, such as beam energy, scanning velocity and focus distance of beam, as well as amount and velocity of particles provide different depths and distribution of particles in the modified layers, from incorporation of particles at the surface of samples exclusively to homogeneous distribution in the remelted layer.

Specimens with rectangular shape in the dimensions 80x100 mm² and 8 mm thickness are prepared from two aluminium alloys AA7075 and AA6082. The chemical composition is given in Tab. 1.

The specimens were processed with laser tracks overlapping 30 - 50%. For processing ROFIN-SINAR diode pumped Nd:YAG laser (DY 044) with maximum beam energy 4.4 kW was applied. Applied process parameters are: laser beam energy density 1200 - 2750 J/cm², specimen traverse velocity 60 - 150 cm/min, protective gas - argon, powder carrier gas - argon 2.3 - 2.5 l/min.
TABLE 1. Chemical composition of investigated aluminium alloys

<table>
<thead>
<tr>
<th>wt-%</th>
<th>Al</th>
<th>Cr</th>
<th>Cu</th>
<th>Fe</th>
<th>Mg</th>
<th>Mn</th>
<th>Pb</th>
<th>Si</th>
<th>Ti</th>
<th>Zn</th>
<th>Other each</th>
<th>Other total</th>
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<tbody>
<tr>
<td>AA 7075</td>
<td>87.1 - 91.4</td>
<td>0.18 - 0.28</td>
<td>1.2 - 2</td>
<td>max 0.5</td>
<td>2.1 - 2.9</td>
<td>max 0.3</td>
<td>-</td>
<td>max 0.4</td>
<td>max 0.2</td>
<td>5.1 - 6.1</td>
<td>max 0.05</td>
<td>max 0.15</td>
</tr>
<tr>
<td>AA 6082</td>
<td>95.1 - max 0.25</td>
<td>0.1</td>
<td>max 0.5</td>
<td>0.6 - 1.2</td>
<td>max 0.4 - 1</td>
<td>max 0.003</td>
<td>0.7 - 1.3</td>
<td>max 0.1</td>
<td>max 0.2</td>
<td>max 0.05</td>
<td>max 0.15</td>
<td></td>
</tr>
</tbody>
</table>

Powder feeding is realized with a cassette type powder feeder. SiC particles (mean size 83 µm) or 50/50 powder mixture of SiC and AlSi40 powder (45 - 90 µm) are used.

The microstructure and phase composition of the modified surface layers were analysed using SEM and EDX; the electrochemical corrosion behaviour of the untreated and the laser treated specimens were evaluated by electrochemical polarisation tests and immersion tests. After dispersing the surface of samples was grinded to provide the same conditions of electrochemical testing for all parameter sets. Electrochemical measurements were carried out in tap water as well as in 3.5% NaCl solution for polarisation curves (potential sweep 1 mV/s).

EXPERIMENTAL RESULTS AND DISCUSSION

Microscopic observations

For adapted process parameters in the near surface layer of the aluminium alloys uniformly distributed reinforcing particles and good surface morphologies can be reached. The main process parameters that influence the properties of obtained layer are laser beam energy density and preheating temperature of specimen, which was in the range from 100 °C to 270 °C in these investigations. In Fig. 1 an example of a dispersed layer obtained by overlapping of single tracks is shown.

Figure 1. Optical micrograph of a typical cross-section (a) and of a top view (b), showing the injected SiC particles; beam energy density 1650 J/cm², A7075 substrate preheat temperature 266 °C, Powder injected SiC:AlSi40 50:50.

Laser treatment due to extremely rapid solidification velocities results in the formation of a fine grain structure within the remelted layer. The bulk material contained relatively large precipitates, as an intermetallic second phase. In the remelted layer there is an intermetallic phase with very fine distribution forming the cell borders of the dendrite structured matrix.

Reinforcing particles are relatively uniformly distributed in the modified layers. Bonding to the matrix material is very good. With increase of the process temperature the depth of
dispersed layers increases. At the same time the stronger dissolving of SiC particles with further forming of very brittle plate-form Al₄C₃ crystals takes place.

**Immersion test**

In order to compare directly the effect of aggressive solution on particular areas of treated material i.e. remelted layer, heat affected zone and bulk material cross-sections of the samples were immersed for 500 hours in 0.5 M NaCl at room temperature. Each 24 hours samples were thoroughly rinsed with distilled water, dried in an oven and underwent SEM investigations. The results are shown in Fig. 2.

Fig. 2. Cross-section of A7075 (a, c) and A6082 (b, d), laser dispersed surface layers (a, b) and bulk material (c, d) after 500 hours of immersion in 3.5% NaCl.

It is seen that for A7075 aluminium alloy large pits are present in the bulk material (Fig. 2, c, d) and are not observed in the remelted layer. The layer of corrosion products is much more uniform and thin. However, at the same time a pit initiation takes place in the remelted layer of A7075 alloy mainly in the places of appearance of intermetallic phase (Fig. 2, a). Pit dimensions in this case are significantly smaller and thinner than that in the bulk material. Boundaries of dispersed SiC particles remain not corroded. In the case of A6082 alloy corrosion in bulk material is also initiated at the places of intermetallic phase. After laser treatment these are very finely distributed on the boundaries of fine crystallites and slight corrosion damage can be observed along the boundaries in the form of thin cracks in uniform layers of corrosion products (Fig. 2, b).
Electrochemical measurements

Electrochemical investigations of A7075 specimens with dispersed layers formed under different treatment conditions show no significant difference of corrosion potential after 24 hours of immersion in 3.5% NaCl solution and the values are in the range 740 - 770 mV. Increase of immersion time to 72 hours does not have considerable effect on the mean values (Tab. 2, Fig. 3).

**TABLE 2. Chance of corrosion potential and corrosion current of aluminium alloy A7075 in initial state and after laser dispersion**

<table>
<thead>
<tr>
<th></th>
<th>-E, mV</th>
<th>i, mA/cm²</th>
<th>-E, mV</th>
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<th>-E, mV</th>
<th>i, mA/cm²</th>
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<tr>
<td>matrix material</td>
<td>600</td>
<td>2.4×10⁻⁶</td>
<td>530</td>
<td>8.5×10⁻⁸</td>
<td>510</td>
<td>8.6×10⁻⁸</td>
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<tr>
<td>1</td>
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<td>530</td>
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<td>6.5×10⁻⁶</td>
<td>630</td>
<td>6.5×10⁻⁸</td>
<td>500</td>
<td>9.0×10⁻⁸</td>
</tr>
<tr>
<td>3</td>
<td>820</td>
<td>5.8×10⁻⁶</td>
<td>710</td>
<td>7.3×10⁻⁸</td>
<td>560</td>
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<td>3.5% NaCl</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>matrix material</td>
<td>760</td>
<td>3.3×10⁻²</td>
<td>780</td>
<td>5.5×10⁻³</td>
<td>790</td>
<td>8.2×10⁻³</td>
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<tr>
<td>1</td>
<td>770</td>
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<td>780</td>
<td>5.5×10⁻³</td>
<td>820</td>
<td>4.2×10⁻³</td>
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<tr>
<td>2</td>
<td>750</td>
<td>2.7×10⁻³</td>
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<td>6.5×10⁻³</td>
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<tr>
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<td>740</td>
<td>4.5×10⁻⁴</td>
<td>780</td>
<td>4.4×10⁻³</td>
<td>780</td>
<td>3.7×10⁻³</td>
</tr>
</tbody>
</table>

1. Laser dispersing without specimen preheating, beam energy density 1100 J/cm²
2. Specimen preheating 266 °C, beam energy density 1650 J/cm²
3. Specimen preheating 170 °C, beam energy density 1650 J/cm²

After immersion in tap water media for all investigated materials some passivation effect was observed. The value of corrosion potential shift increases with increasing the preheating temperature of samples.

Corrosion potentials of this alloy measured in tap water for different laser treatment parameters show more positive values compared to that obtained in 3.5% NaCl solution. With
the increase of immersion time to 72 hours potential stabilises at values 500 - 560 mV. Shift of corrosion potential with prolonged immersion is much smaller in the case of aggressive media than in tap water (Fig. 4, Tab. 2).

Fig. 4. Change of corrosion potential of aluminium alloy A7075 in initial state (matrix) and after laser dispersion in tap water:
1 - Laser dispersing without specimen preheating, beam energy density 1100 J/cm²
2 - specimen preheating 266 °C, beam energy density 1650 J/cm²
3 - specimen preheating 170 °C, beam energy density 1650 J/cm²

Values of corrosion current densities of the modified surface layers of A7075 alloys in 3.5% NaCl solution lay in the range from 3.3·10⁻² to 4.5·10⁻⁴ mA/cm² (Tab. 2, Fig. 4). At the same time corrosion rate in tap water is approximately two orders of magnitude lower than that in NaCl solution ($i_{corr}$ = 2.5·10⁻⁴ - 2.8·10⁻⁶ mA/cm²). For measurements in tap water as well as in 3.5% NaCl solution no significant influence of laser dispersing processing on the corrosion rate is detected.

Corrosion potentials of A6082 aluminium alloy in as received conditions as well as after laser dispersing measured in 3.5% NaCl solution practically are the same and after 48 h immersion in corrosive media a slight shift in negative direction of approximately ~ 20 - 30 mV is observed (Tab. 3).

Values of corrosion potential measured in tap water are more positive. Besides laser treatment leads to a certain decrease of corrosion potential from -460 mV for as received material to -500 mV for dispersed layers containing SiC particles. After 48 hours immersion of modified layers further decrease of corrosion potential to -530 mV is noted. At the same time for non treated material a shift of 80 mV to positive values is measured, which indicates some passivation process on this surface.
Fig. 5. Current density/potential curves for aluminium alloy A7075 after laser dispersion and 1h of immersion in tap water (a) and 3.5% NaCl solution (b)
1 - Laser dispersing without specimen preheating, beam energy density 1100 J/cm²
2 - specimen preheating 266 °C, beam energy density 1650 J/cm²
3 - non treated bulk material

TABLE 3. Change of corrosion potential and corrosion current density of aluminium alloy A6082 in initial state and after laser dispersion with specimen preheating 266 °C, beam energy density 1650 J/cm²

<table>
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<tr>
<th></th>
<th>immersion time</th>
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<td></td>
<td>1 h</td>
<td>24 h</td>
<td>48 h</td>
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</tr>
<tr>
<td></td>
<td>-E, mV</td>
<td>i, mA/cm²</td>
<td>-E, mV</td>
<td>i, mA/cm²</td>
</tr>
<tr>
<td>tap water</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>matrix material</td>
<td>460</td>
<td>1.1·10⁻⁴</td>
<td>420</td>
<td>1.7·10⁻⁴</td>
</tr>
<tr>
<td>modified layer</td>
<td>500</td>
<td>6.7·10⁻⁵</td>
<td>550</td>
<td>5.9·10⁻⁴</td>
</tr>
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<td></td>
<td></td>
</tr>
<tr>
<td>3.5% NaCl</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>matrix material</td>
<td>680</td>
<td>1.8·10⁻⁴</td>
<td>690</td>
<td>2.5·10⁻³</td>
</tr>
<tr>
<td>modified layer</td>
<td>690</td>
<td>4.0·10⁻³</td>
<td>690</td>
<td>3.2·10⁻³</td>
</tr>
</tbody>
</table>

CONCLUSION

1. Laser met injection of reinforcing SiC particles provides formation of surface layers in aluminium alloys with fine dispersed microstructure and uniform distribution of intermetallic phases along the cell boundaries of the aluminium solid solution. Injected silicon carbide particles demonstrate good bonding to matrix material. Pitting formation in the modified layers of A7075 alloy was not completely avoided by laser processing, but the dimensions of separate pits are considerably reduced.

2. For A6082 alloy an influence of laser treatment is more noticeable for the case of immersion in tap water compared to corrosive 3.5% NaCl solution media. In spite of the fact that corrosion potential is more negative, corrosion current density is in the same range of values.
REFERENCES