A REACTION COATING ON ALUMINIUM ALLOYS BY LASER PROCESSING

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Introduction

Aluminium alloys are widely applied mainly because of their high strength/weight ratio and corrosion resistance in most circumstances. However, the surface properties of aluminium alloys, in particular the hardness and wear resistance are insufficient to fulfil many requirements. Surface coating with ceramics can be a very promising approach to overcome this problem. By means of high power laser, very high temperature can be reached to melt both the metal substrate and ceramic coating, which may promote chemical reaction and wetting between ceramic and metal, and as a result may lead to a strongly bonded ceramic/metal interface after re-solidification [1]. However there are several difficulties for laser coating on aluminium alloys with ceramics. The high melting point of ceramics (\(\text{Al}_2\text{O}_3\) 2030 °C, \(\text{SiO}_2\) 1720 °C) requires a high laser energy density to melt ceramics which may lead to strong convection in the aluminium molten pool as the melting temperature of aluminium alloy is rather low (600-650 °C). It may destroy the bonding between metal and ceramic. Another difficulty is that the large difference of thermal expansion between aluminium (22 µm/m°C) and ceramics (\(\text{Al}_2\text{O}_3\) 8 µm/m°C, \(\text{SiO}_2\) 0.5 to 3 µm/m °C) [3] can cause large interface mismatch during the rapid solidification which may damage the interface bonding. Therefore a careful selection of laser parameters and ceramic-metal system are crucial.

The idea to choose \(\text{SiO}_2\) to coat on aluminium alloys are mainly the following three aspects. First, aluminium or its oxide adheres firmly to a glass and the aluminium/glass bond is stronger than the glass [2]. The glass spread rapidly on the oxidized surface and the affinity is so strong that molten glass climbs onto the surface of a vertical metal plate. These results imply that there exist a good wetting and firm adhesion between aluminium and \(\text{SiO}_2\). Secondly, aluminium reacts with \(\text{SiO}_2\) to form \(\text{Al}_2\text{O}_3\) already at 400 °C. The \(\text{Al}_2\text{O}_3\) may overcome some drawbacks from \(\text{SiO}_2\), that is very brittle and has a low thermal expansion coefficient. Furthermore the large amount of heat from the exothermic reaction between Al and \(\text{SiO}_2\) may help further heating of the oxide.

Experiments

Pure aluminium and a commercial alloy Al6061 (1.0 wt% Mg, 0.6 wt% Si, 0.25 wt% Cu and 0.25 wt% Cr) were used as substrate materials. A mixture of silicate \(\text{SiO}_2\) and pure aluminium powders with a mole ratio of 1:1 was used to coat both pure Al and Al6061. The size distribution of the particles peaked around 50 µm and 60 µm, respectively. In addition \(\text{Al}_2\text{O}_3\) powder was also used to coat these materials for the sake of comparison. The size of the \(\text{Al}_2\text{O}_3\) powder ranged from 5 to 20 µm.

A CW-CO\(_2\) Spectra Physics 820 laser was operated with a defocus beam of 10 to 20 mm and power of 400 to 1200 W. The laser beam diameter was 1.5 to 3.0 mm and the trace overlap was 67%. The scan velocity of the beam with a moving table was 15 mm/s and the substrate was water cooled. The laser processing was employed by a home-made powder feeding system under Ar shielding atmosphere. When sufficient thickness of coating was
required, several subsequent layers were coated on the substrate. The crystallographic phases of the original powders and the coatings were determined by X-ray diffraction using CuKα radiation. After the laser treatment, a transverse cross section was made for inspection in a Scanning Electron Microscopy (SEM) with Energy Dispersive X-ray spectrometry (EDS) for composition analysis.

**Experimental results**

In figure 1 the X-ray diffraction spectra of the coating is depicted. After laser processing of the powder mixture of SiO₂ and Al on aluminium alloys, α-Al₂O₃ phase and Si phase have been formed. Because many of the strong peaks from mullite (Al₄Si₂O₇) are overlapping with those of α-Al₂O₃ and SiO₂, only a few peaks might be used for indexing of mullite. The diffraction peaks of spinel (MgAl₂O₄) coated on Al6061 with both SiO₂ and Al₂O₃ powders are also very weakly present. Some SiO₂ peaks are still detectable, probably because some not-melted SiO₂ powders were dropped on the coating.

![X-ray diffraction spectrum of laser coating on Al6061 with SiO2 and Al powders.](image)

The coating on pure aluminium substrate presented a similar behavior as that on Al6061. The difference was that there was a high concentration of magnesium along the interface between the oxide coating and Al6061 substrate which can be concluded from table 1.

**Table 1**

<table>
<thead>
<tr>
<th>Position</th>
<th>Mg</th>
<th>Al</th>
<th>Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>hard layer</td>
<td>0–0.05</td>
<td>35–40</td>
<td>1.5–3.2</td>
</tr>
<tr>
<td>soft layer</td>
<td>0.05–0.32</td>
<td>29–32</td>
<td>9–10</td>
</tr>
<tr>
<td></td>
<td>0–0.1</td>
<td>0.05–6.6</td>
<td>15–31</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>9–26</td>
<td>15–31</td>
</tr>
<tr>
<td>substrate</td>
<td>0.5–0.99</td>
<td>1.8–3.4</td>
<td></td>
</tr>
<tr>
<td>M/O interface</td>
<td>3.1–3.5</td>
<td>1.4–2.5</td>
<td></td>
</tr>
</tbody>
</table>

SEM micrographs taken from a transverse cross section of the oxide coating on Al6061 alloy are displayed in figure 2. A homogeneous layer of 100 μm thickness was formed. This reaction layer has a similar composition as Al₂O₃ in which the silicon content is rather low ranging from 1.5 to 3.2 mole%. In the reaction coating sometimes a
few aluminium spherical particles can be seen together with silicon precipitated inside. Some typical interface structures are represented in figure 2a to 2e. Across the interface with the substrate there are two intermediate layers: a hard reaction Al₂O₃ layer (white) in contact with the aluminium substrate and a soft layer (dark) with a high silicon content lying between the hard layer and the Al₂O₃ reaction coating (white) (figure 2c). There exists an extensive composition fluctuation over the soft layer as listed in table 1.

FIG. 2 Transverse cross section of a reaction layer on Al6061 with SiO₂ and Al powders by laser coating. (a) A dense and thick layer of 100 μm. (b) A rough metal/oxide interface as Al₂O₃ particles exist in the Al6061 substrate. (c) Two intermediate layers of a reaction Al₂O₃ layer (white) and a high Si content layer (dark) between substrate and oxide coating. (d) A thin Al₂O₃ layer (white) and some silicon spherical precipitates in the high Si content layer (dark). (e) Aluminium from substrate flew into an Al₂O₃ reaction layer.

FIG. 3 A transverse cross section of an Al₂O₃ layer on Al6061 with Al₂O₃ powder.
Some of the soft layers consist of a composition as Mullite $\text{Al}_2\text{Si}_2\text{O}_7$ (28.6 mole% Al and 9.5 mole% Si) and some are approximately at the eutectic composition (1.6 mole% Al and 32 mole% Si) in the $\text{SiO}_2$-$\text{Al}_2\text{O}_3$ [12]. Spherical silicon precipitates were detected inside the soft layer, see figure 2d. The thickness of the soft layer ranged from zero to 10 $\mu$m. If it is zero as shown in figure 2e the whole coating become an $\text{Al}_2\text{O}_3$ reaction layer. In this figure a good wetting can be seen between aluminium and the aluminium oxide. The hard intermediate $\text{Al}_2\text{O}_3$ layer can be very thin down to 1 $\mu$m. Most of the interfaces between aluminium substrate and the $\text{Al}_2\text{O}_3$ reaction layer, and between soft layer with high silicon content and $\text{Al}_2\text{O}_3$ layer are firmly joined. However sometimes voids can be observed at the oxide/metal interface from figure 2a, but no crack along the interface is observed.

The micro-hardness measured from the reaction layer of $\text{Al}_2\text{O}_3$ ranges from $H_Vo_2$ 2300 to 3060 which is equivalent to the value of $H_Vo_2$ 2100 - 2720 [3] of alumina ($\text{Al}_2\text{O}_3$) and is much larger than $H_Vo_2$ 820 of quartz ($\text{SiO}_2$).

Figure 3 shows a thin coating from $\text{Al}_2\text{O}_3$ powder on Al6061. Debonding along the oxide/metal interface can clearly be seen. Only a very thin layer can be formed independent as to how high laser intensity was applied. In this coating a four times higher laser energy density with a small beam was employed comparing to the formation of a 100 $\mu$m thicker layer with $\text{SiO}_2$ and Al powders.

Discussion

According to the X-ray diffraction and EDX results the following reaction has occurred during laser coating on aluminium alloys with the powder mixture of $\text{SiO}_2$ and Al: $2 \text{Al} + 3/2 \text{SiO}_2 = \text{Al}_2\text{O}_3 + 3/2 \text{Si}$.

The free energy of the reaction is $-297.7$ kJ/g.mole at 1173 °K as calculated according to the data presented in [4]. The heat from this exothermic reaction is about 383.4 kJ/g.mole at 1173 °K. Suppose that the reaction starts at 1173 °K, then the amount of heat required to heat and melt the reaction products of one mole $\text{Al}_2\text{O}_3$ and 3/2 mole Si to 2300 °K (the melting point of $\text{Al}_2\text{O}_3$) is calculated as 266.6 kJ/g.mole and 80.7 kJ/g.mole, respectively. Therefore the amount of the reaction heat is sufficient to melt the products of $\text{Al}_2\text{O}_3$ and Si starting from about 1173 °K. This result indicates that the $\text{SiO}_2$ powder and Al only need to be heated to about 1173 °K by the laser beam, and then the coating of the reaction product $\text{Al}_2\text{O}_3$ can be heated and melted spontaneously by the exothermic reaction. Consequently, this coating processing can be addressed as a reaction coating. However, comparison with the laser energy employed, the heat from the exothermic reaction is relative small in the order of 10% of the absorbed laser energy, assuming an absorption coefficient of 0.5 of the laser beam, a layer thickness of 100 $\mu$m and the laser parameters described in the experimental part. Nevertheless, the reaction heat seems to be very efficient for the formation of the ceramic layer, as much less laser energy density is required to form a coating with a reactive powder of $\text{SiO}_2$ and Al compared with the non-reactive powder of $\text{Al}_2\text{O}_3$. This may be due to the reaction which is much faster and more localized in the oxide coating than in the metal pool.

Instead of saving the laser power, the heat from the reaction can also help to reduce the convective flow inside the aluminium melt pool. It is known that a convection in a laser melt pool is caused by a positive surface energy gradient with respect to temperature from the center to the edge of the pool, i.e. the temperature with a Gaussian profile of the laser beam is much higher in the center than near the edges. In general, the higher the laser energy density, the stronger the convection. Further, it can be imagined that the convection in the melt pool may cause cracks perpendicular to the surface in a ceramic coating and increases the roughness of the coating [1]. In contrast the heat from the exothermic reaction may distribute homogeneously over the melt pool and may contribute to the convection only slightly. Therefore if an exothermic reaction occurs, a lower laser energy density may be applied which may induce a weaker convection and further may form a more homogeneous more crack free ceramic coating. However, a too large amount of heat flow from the reaction will strongly disturb the melt pool and causes cracks and an increase of roughness of the coating. This was often found in our experience and it will be more severe if the reaction and temperature are inhomogeneously distributed. The powder size and mixing, the stability of powder feeding, the substrate temperature or cooling, as well as the laser process parameters such as laser power, scan velocity and beam diameter, will all significantly affect the reaction, and should be very carefully controlled.
It is suggested [5,6,11] that the exothermic heat of a chemical reaction may contribute to a metal/ceramic interface energy and improves wetting between them [5]. According to our experiments, the wetting between oxide and metal seems to be improved significantly by the reaction since a good adhesive layer was formed on aluminium alloys with the reactive powder of SiO2 and Al but not with Al2O3 powder. However Laurent et al.[5] presented a different result, namely that the effect of the reaction on wetting was impossible to see as the final wetting angle of Al on SiO2 is about 68° which is near to 64° of Al on Al2O3. The reason suggested by them is that the reaction precedes the wetting and consequently the contribution of the free energy of the reaction to the wetting is negligible. The different result presented here is not clear as the wetting process during reaction is not yet well established [9,11].

All SEM pictures of the cross section of the Al2O3 reaction coating indicated that the oxide was melted. The silicon concentration in the coating is rather low of about 1.5-3.2 mole%, which means that the solubility of silicon in aluminium oxide is low and most silicon diffused into aluminium substrate from the molten oxide. A few spherical aluminium precipitates existed in the reaction Al2O3 coating, and silicon mostly precipitated inside the aluminium particles. This is because the interface energy of Al/Al2O3 and Al/Si is lower than that of Si/Al2O3. The feature of two intermediate layers, a thin aluminium oxide layer in contact with an aluminium substrate and a high silicon content oxide layer lying between the thin layer and the aluminium oxide reaction coating, can be interpreted by the diffusion processes of Si into aluminium substrate and Al into oxide. The reaction rate appeared to be controlled by atom diffusion mechanism [7]. The diffusion coefficient of aluminium and oxygen in poly-crystalline Al2O3 are about 10^{-11} cm²/sec and 2.10^{-12} cm²/sec at 2000°K, respectively which are much lower than 10^{-8} cm²/sec of silicon in 40CaO20Al2O3-40SiO2 (lack of data in Al2O3) at 2000 °K [8]. The diffusion of oxygen in oxide is too slow and can be neglected.

During laser processing the aluminium substrate reacted with silicon oxide at interface and formed a thin aluminium oxide layer and at the same time most of silicon in the coating will diffuse through this molten layer into aluminium substrate as the diffusion rate of silicon in the oxide is much faster than that of aluminium. However after the thin aluminium oxide layer solidifies, both silicon and aluminium can hardly diffuse through it within a short period, say 0.1 second, as the diffusivity in solid is much lower than in liquid. The diffusion distances of silicon in 40CaO-20Al2O3-SiO2 and aluminium in Al2O3 at 2000°K are (2Dt)^1/2= 4.5 μm and 0.01 μm respectively in 0.1 second taking the afore-mentioned diffusion data. Then the silicon coming from the top coating may accumulate and form a high silicon content oxide layer in front of the thin aluminium oxide layer. It may even form precipitates when the solution of silicon becomes saturated in the oxide layer. The latter was observed in the SEM picture (Fig. 2d).

The high concentration of Mg along the Al/Al2O3 interface on Al6061 may indicate the existence of MgO and MgAl2O4 spinel phases which was reported by many other researchers [13]. The formation of spinel might promote the metal/oxide wetting [1]. However, the low boiling point of 1107 °C of Mg, which could be one reason of Mg segregation at interface, may be detrimental for the formation of a good bonded oxide layer because it disturbs the melt pool. Therefore, an aluminium alloy containing a high concentration of Mg should not be chosen to coat by laser processing.

The bond strength of a metal/ceramic interface, especially the shear strength, can be very critical for the formation of a good bonded ceramic coating, as the large difference of thermal expansion coefficients between metals and ceramics can induce high interface (mainly shear) stresses, during the rapid solidification after laser processing. These high stresses can destroy the interface bonding if it exceed the interface strength. However because of lacking data of the shear strength, we will focus on the tensile stress instead. Further, the chemical reaction needed to cause wetting of ceramics also affect interfacial microstructure and hence strengths. It was suggested that the reaction products formed at the interfaces create chemical bridges between the ceramics and metals, and hence the interface strengths are predominated by the interface properties between reaction products and the metals. The tensile strengths of Al/Al2O3 interface have been reported to be very high of about 400 MPa produced by braze joining and of 90 MPa produced by diffusion bonding [9]. The strength of 400 MPa produced by brazing may be a reasonable estimate for our interface of Al2O3 reaction coating on aluminium alloys as the aluminium is melted in
both cases. Comparing with the tensile strength 125 MPa and yield strength 56 MPa of cast Al6061 alloy, this interface strength of 400 MPa is sufficient to keep the interface bond before the aluminium substrate undergoes plastic deformation or even failure.

This argument is in accordance with results presented by Dalgleish et al. [10]. In their work alumina was bonded with liquid Al and Al-4wt%Mg alloy. During mechanical test failure never occurs by interface cracking. Instead, the bond strength is limited either by plastic flow or by ductile fracture in the metal when the bond layer is thick, and by the strength of the alumina if the bond layer is thin. The Al alloy bond has also been shown capable of arresting cracks by plastic blunting. However, Klomp [11] reported that the tensile strength of Al2O3 reaction interface between Al and SiO2 is zero. In our opinion, this zero strength might be caused by the failure of SiO2 itself near the interface of SiO2/Al2O3 but does not reflect the interface strength of Al2O3.

Summary

An aluminium oxide layer of 100 μm in thickness has been successfully coated on aluminium alloy 6061 and pure aluminium using a powder mixture of silicon oxide and aluminium by laser processing. A strong Al/Al2O3 interface was formed. The exothermic chemical reaction between SiO2 and Al may promote the metal/oxide wetting and the formation of Al2O3 layer. This new approach of ceramic coating on metals using a chemical reaction of other ceramics with metals may be applied to other systems.

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References