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The microstructure and corrosion resistance of micro-arc oxidation coatings on SiCp/A356 composites

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Micro-arc oxidation (MAO) coatings were prepared on a SiC_p/A356 composite. The microstructure and phase composition of the coatings on the SiC_p/A356 composite were examined by XRD and SEM methods. It was found that there were two layers in the coating, a dense layer which was mainly composed of crystalline α -Al₂O₃ and a loose layer which consisted of γ -Al₂O₃ and mullite. The coating was well bonded to the SiC_p/A356 substrate. The corrosion behavior of the coated and uncoated SiC_p/A356 composites was evaluated with a salt spray test and a potentiodynamic polarization technique. The results of the salt spray test showed that the coating could improve the corrosion resistance of SiC_p/A356 by 11 times. The corrosion potential was shifted significantly in the anodic direction and the corrosion current density of the coated SiC_p/A356 composite was reduced.

Key words: aluminum matrix composites, micro-arc oxidation, ceramic coating, corrosion.

Introduction

Silicon carbide particulate reinforced aluminum composites (SiC_p/Al composite) have excellent properties such as high specific strength and modulus, good wear resistance, etc. However, the addition of silicon carbide particles increases the corrosion sensitivity because of the existence of the two phases of silicon carbide and Al matrix together with their interface. The corrosion resistance can be improved by applying surface coatings. However, it is difficult to obtain dense coatings using conventional anodic oxidation and chemical passivation because of the existence of nonconductive SiC particles. The micro-arc oxidation (MAO) method has been developed to provide ceramic coatings for aluminum, titanium and magnesium based materials in order to protect them from severe corrosion and wear [1-4]. After micro-arc oxidation treatment, the wear resistance and corrosion resistance of these metals and their alloys can be improved significantly. Although there have been many investigations of the treatment of aluminum, magnesium and titanium alloys using the MAO method [5, 6], little research has been done on SiCp/Al composites using this method till now. In the study reported here, protective coatings were successfully fabricated on $SiC_p/A356$ composites by a MAO method. The microstructure and composition of the coatings were investigated using SEM and XRD methods and the corrosion resistance of the coatings was tested as well.

Experimental Details

20% vol. SiC_p/A356 composites manufactured by stir casing were used as substrates. Samples with dimensions of a diameter $\Phi 40$ mm and a thickness of 10 mm were anodized with a 75 kW MAO instrument which consists of a special high voltage AC power supply with asymmetric potential peak waveform at anode and cathode and a stainless steel bath with a stirring and cooling system.. In the experiment, the samples and the stainless steel walls of the bath were used as the two electrodes. The electrolyte was prepared from a solution of sodium aluminate in de-ionized water with sodium silicate. The electrolyte temperature was controlled to be lower than 45 °C during the oxidation process. The current density was varied in the range of 1000-1200 A/m^2 . The treatment time was chosen to produce a coating thickness of 80 µm. After the MAO processing, the samples were rinsed in distilled water and dried in hot air.

The morphology and microstructure of the MAO coatings were observed by a JSM-5800 scanning electron microscope (SEM). Because of the low conductivity of MAO coatings, the samples were sputter-coated with gold prior to SEM observation. The phase structures of MAO coatings were investigated by a Rigaku D/Max2200 X-ray diffractometer (Cu target, 40 kV, 40 mA).

The corrosion resistance of the coated and uncoated $SiC_p/A356$ composite samples were evaluated by both

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a salt spray corrosion test and an electrochemical corrosion test. The salt spray test was performed in accordance with the GB/T 10125-1997 standard. In this test, samples with their edges protected by epoxy resin were placed in a cabinet at 35 °C for 120 hours under an aqueous spray (a solution of 5 wt.% NaCl in distilled water). The samples were observed at regular intervals and the time taken for the first appearance of a corrosion spot on the surface was recorded. The corrosion rate ΔW was used to evaluate the corrosion resistance of coated and uncoated SiC_p/A356 composite. The corrosion rate is defined by $\Delta W=(W_1-W)/W\times100\%$, where W stands for the sample mass before salt spray corrosion test and W_1 stands for the sample mass after the salt spray corrosion test.

The electrochemical corrosion tests were carried out in a 3.5 wt.% NaCl solution in a three-electrode cell by a M283 model potentiostat. Samples were embedded in an epoxy resin in order to ensure the exposure of a similar surface area of 1 cm^2 to the corrosive electrolyte. A copper wire that was used to conduct current flow was soldered on the back of the sample and completely covered by the epoxy resin. The SiC_p/A356 composite samples without the MAO coating were polished to a 1 μ m finish. Samples with MAO coatings were tested without any further mechanical or chemical surface treatment. A commercial Pt electrode was used for the counter electrode and a saturated calomel electrode (SCE) for the reference electrode. Before the potentiodynamic test, the samples were kept in the NaCl solution for at least 1 hour to stabilize at their corrosion potential. After that, the polarization scan was started below the steady open-circuit potential in the cathodic direction at a scanning rate of 1 mV s⁻¹.

Result and Discussion

Microstructure and phase analysis

The surface morphologies of MAO coatings are shown in Fig. 1. The surfaces of the MAO coatings were porous and rough. Crater-shaped grains that are caused by the micro-sparks during the MAO process are the



Fig. 1. Surface morphologies of a MAO coating formed on the $SiC_p/A356$ composite, (b) is a magnification of (a).



Fig. 2. Cross-section morphologies of a MAO coating on a SiC_p/A356 composite.

main characteristics of MAO coatings. As shown in Fig. 1b, the trace of rapid solidification of molten alumina can be clearly observed on this surface and it can be predicted that the instantaneous temperature in the microarc zone reaches several thousand degrees Celsius. It can also be seen that discharge channels are not distributed uniformly on the coating surface. This phenomenon results from the different current conductivity of silicon carbide particulates and the aluminum matrix.

Figure 2 shows the cross sectional morphologies of MAO coatings on SiC_p/A356 composite. The MAO coating is about 90 μ m thickness and consists of two layers, a loose layer of 20 μ m and a dense layer of 70 μ m thickness. The interface is clear and there is no obvious transition layer between the SiC_p/A356 substrate and the dense layer. It can also be seen that the combination of the substrate and the dense layer appears with a very rough morphologies, which shows that the MAO coatings have good adhesive properties to the substrate. The energy dispersive Xray spectrometer (EDS) result collected from the coating surface shows that it is mainly composed of oxygen ,aluminum and silicon with its elemental contents of 31.27%, 55.84% and 12.89% respectively.

An XRD pattern of a MAO coating is shown in Fig. 3. The structure of the coating is crystalline and mainly consists of a mixture of α -Al₂O₃ and γ -Al₂O₃ and mullite, which is different from that achieved by conventional anodizing. The XRD result is in accordance with the EDS results. During the micro-arc oxidation process, the instantaneous temperature in the spark or microarc zone is high enough to create amorphous aluminum oxides to melt. The molten alumina is solidified to form α -Al₂O₃ and γ -Al₂O₃ and other phases. The difference in the cooling rate of the molten alumina in the micro-arc zone results in different contents of γ -Al₂O₃ and α -Al₂O₃ between the external and internal



Fig. 3. XRD pattern of a MAO coating on the $\mathrm{SiC}_{p}/\mathrm{A356}$ composite.

layers of a coating. The higher cooling rate at the external layer of a coating promotes the formation of the γ -Al₂O₃ phase. By contrast, the α -Al₂O₃ phase is easily formed in the internal layer at a lower cooling rate [7].

Corrosion resistance

Table 1 provides data on the salt spray resistance of the coatings. The time for the first appearance of corrosion spots on the coating surface in the test procedure was recorded. It is clear that the coated $SiC_p/A356$ composite gives an almost impenetrable coating with-

Table 1. Salt spray test results on coated and uncoated $SiC_{p}\!/$ A356 composites

Samples	Time (in hours) for first appearance of corrosion	Corrosion rate /%
uncoated SiC _p /A356 coated SiC _p /A356	12 >120	0.141 0.012
could brop 1550	> 120	0.012



Fig. 4. Morphologies of the (a) uncoated and (b) coated SiC_p/A356 composites after 120h exposure to the salt spray test.

Table 2. Results of the potentiodynamic corrosion tests in a 3.5 wt% NaCl solution

Samples	Ecorr /V	Icorr/(uA/cm ²)	Anodic Tafel slope	Cathodic Tafel slope
Uncoated SiC _p /A356	-0.720	3.09	3.8	2.108
Coated SiC _p /A356	-0.681	1.65	4.173	4.265



Fig. 5. Potentiodynamic polarization curves for coated and uncoated $SiC_p/A356$ composites in a 3.5% wt NaCI solution.

out any sign of corrosion after 120 hours exposure, while corrosion spots appeared on the uncoated SiC_p/A356 composite only after about 12 hours. After 120 hours salt spray test, the corrosion rate of the coated SiC_p/A356 composite is more than 11 times lower than that of the uncoated SiC_p/A356 composite. Figure 4 shows morphologies of the surface of uncoated and coated SiC_p/A356 composites after exposure to the salt spray test. It can be seen that pits appeared on the surface of the uncoated SiC_p/A356 composite while there is no corrosion of the coated SiC_p/A356 composite.

Figure 5 shows the polarization curves of the coated sample and uncoated $SiC_p/A356$ substrate. The corrosion potentials, corrosion rates, anodic and cathodic Tafel slopes were calculated from these tests. A summary of the results of the potentiodynamic corrosion tests is given in Table 2. The coated $SiC_p/A356$ composite possesses a much higher corrosion potential and lower corrosion rate than an uncoated SiC_p/A356 composite sample. The corrosion potential Ecorr increased from -720 mV of the SiC_p/A356 substrate to -681 mVof the coated SiC_p/A356 composite. Also, the current density of the coated SiCp/A356 composite decreased from 3.09 uA/cm² to 0.165 uA/cm². These data indicate that MAO coatings can improve substantially the corrosion resistance of SiC_p/A356 composites. Although the surface of the MAO coating is porous, the dense crystalline layer in the coating can act as a barrier to prevent the $SiC_p/A356$ from environmental corrosion.

Conclusions

A protective coating was successfully fabricated on $SiC_p/A356$ by a MAO method. The surface of the MAO coating was porous and rough. The MAO coating was mainly composed of two layers, a dense layer of 70 µm thickness and a porous layer of 20 µm thickness. The XRD pattern showed that the coating was crystalline and mainly consisted of a mixture of α -Al₂O₃ and γ -Al₂O₃ and mullite. Salt spray tests showed that the corrosion rate of the coated SiC_p/A356 composite was about 11 times lower than that of the uncoated SiC_{p} / A356 composite after 120 hours exposure to a salt solution. Electrochemical tests showed that the coated SiC_p/A356 composites possessed a much higher corrosion potential and a lower corrosion rate than the uncoated SiC_p/A356 composite. Both the salt spray tests and the electrochemical tests showed that MAO coatings could improve the corrosion resistance of SiC_p/A356 significantly.

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