

EFFECT OF HEAT TREATMENT ON PITTING CORROSION RESISTANCE OF 6061 Al/SiC_p COATED BY THE CERIUM OXIDE FILM IN 3.5 N NaCl SOLUTION

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Introduction

The traditional material for the construction of ship and submarine hulls is steel, with aluminum and aluminum based composites used, in particular, for weight sensitive applications [1–3]. Aluminum metal matrix composites have high ratios of the Young modulus/density and yield strength/ density as well as tailability coefficient of thermal expansion and high thermal stability conductivity; hence they look very promising and find applications in marine industries [5–6]. However, one of the main drawbacks of aluminum matrix composites is the decrease in corrosion resistance compared to the base alloy. Various surface modification procedures are being evaluated for Al alloys and their composites to improve the corrosion resistance. Some chromate-free processes have been investigated to improve the corrosion resistance of Al based metal matrix composites. Many alternatives to chromium corrosion protection systems have been investigated, but few offer the protectiveness or easy application of chromate coatings. Among potential chromate replacements, mostly rare-earth compounds, particularly cerium compounds, have attracted significant attention [7–9]. Cerium dioxide (CeO₂) film has been deposited using such techniques as electrochemical deposition, reactive magnetron sputtering, electron beam evaporation, metal-organic chemical vapor deposition, pulsed laser deposition and sol-gel. The electro-chemical processing has been regarded as a potential technique for the preparation of high performance materials. The advantages of this process include the purity of reagents, the control of the homogeneity for precursor mixtures, the potential control of the phase evolution and microstructure, and the opportunity for fabrication of materials into useful non-traditional shapes [9–11]. The objective of the present paper is to investigate the effects of aging on the corrosion behavior of 6061 Al/SiC_p composite and of heat treatment temperature on the microstructure and corrosion behavior of cerium oxide coatings prepared by chemical bath technique on 6061 Al/SiC composite in 3.5 N NaCl solutions, by means of potentiodynamic polarization technique.

Experimental procedure

The material used in this study was a 15% volume fraction of SiC_p particle reinforced 6061 Al composite fabricated by stir casting technique. The composite was made of 6061 Al alloy reinforced with particulate SiC (99.9% purity) and 23μm size. The composite in the form of cylinders was cut into dimensions 20x20x20 mm, prepared for the Brinell hardness measurements (ASTM E10). All specimens were solution treated at 558°C for 1 hour, water quenched, and then aged at T 140, 160, 180, 200, 220 and 240°C for various durations of time (T6 treatment). The age-hardening response of the composite was characterized using the Brinell hardness measurements. Based on the hardness profile, the aged samples were classified into three categories, namely, ‘under aged’, ‘peak aged’ and ‘over aged’. The aged samples were subjected to electrochemical measurements in 3.5N NaCl solution. The peak aged samples were found to corrode more as compared to other aged samples. Hence, the peak aged samples were selected for cerium oxide coatings in order to improve the corrosion resistance. Before treatment, the peak aged sample surfaces were polished by 2000-grit silicon carbide (SiC) abrasive papers. Then, a chemical pretreatment of the peak aged composites was carried out as follows: “degreasing treatment” by immersion in an aqueous solution of NaOH at pH 12 for 1 min at room temperature. After the chemical pretreatment, a cerium based conversion coating was obtained on the pretreated samples by immersion in cerium solution for 30 min at 30 °C.

The solution pH was adjusted to 2.85 with NaAc + HAc and was kept constant during the coating processes. Rinsing with deionized water was performed after each step (pretreatment and conversion). A typical coating solution was prepared by dissolving 7.5 g CeCl₃ into 1000 ml of deionized water with H₂O₂ concentration (Ce:H₂O₂ molar ratio of 1:50)100 ml/L. The pretreated samples were dipped into the coating

solution for 30 minutes and then dried in an open air atmosphere. Before heat treatment, the samples were dried at ambient temperature for 2 h and then subjected to heat treatment at 300 °C, 400 °C, and 500 °C for 30 min, respectively. The rate of raising and falling temperature was about 1 °C/s.

Electrochemical measurements were performed with a potentiostat under software control (CH Instrument, USA Model 604 A). Polarization scans were initiated from 300 mV and scanned to approximately -1100 mV, all potentials being correlated to the open-circuit corrosion potential. Polarization curves were recorded over the range of 300 to -1100 mV, from which corrosion rates were estimated. All potentiodynamic scan rates were 0.33 mV/s. Electrochemical cell was composed of a glass five-neck flask, a large area platinum counter electrode, and saturated calomel electrode (SCE) as a reference electrode. All potentials were referenced to the SCE. Polarization resistance measurements were conducted via potentiodynamic polarization measurements. Tests were performed at room temperature in 3.5N NaCl solution. The exposed area of the samples was about 1 cm². The potential scan was started 10 min after the specimens were placed into the test solution when they reached a steady open circuit potential. The SEM and the XRD analyses were used to characterize the surface morphology and composition features.

Results and discussion

Effect of aging on corrosion behavior of the composite

Hardness-time curves of artificially aged 6061 Al composite of 15 vol. % SiC_p at different temperatures are shown in Fig. 1. The general shape of the aging curves for all samples aged at different temperatures shows a similar trend, i.e. the hardness increases gradually with the increase of the ageing time at the initial stage, then, after reaching the peak hardness, there is a decreasing trend observed in hardness. The ageing temperature does not affect the sequence of aging, but affects the magnitude of the peak hardness achieved. At 180 °C the peak hardness is maximal. At aging temperatures lower than 180 °C, the peak hardness is achieved within a shorter ageing period while at aging temperatures above 180 °C, the peak hardness is achieved within a longer ageing time. But in both cases the magnitude of peak hardness is lower than its value achieved at 180 °C. Figure 2 plots the variation of peak hardness vs. ageing temperature. The peak hardness profile shows that the specimens were under aged at T below 180 °C, peak aged at T 180 °C and over aged at T above 180 °C. Depending on the phase transformation and ageing kinetics, the peak hardness achieved varies with respect to the duration and temperature of the ageing process.

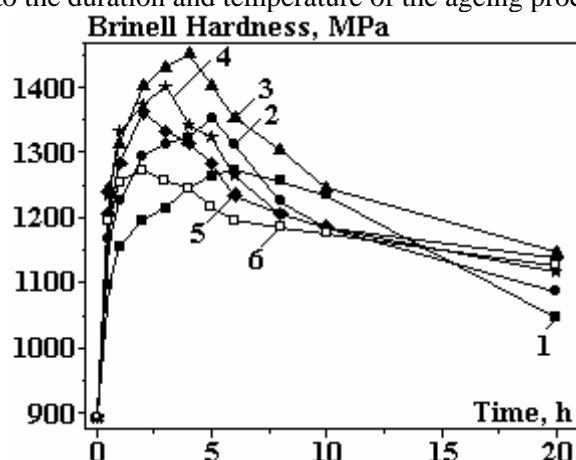


Fig. 1. Hardness variation with ageing temperature and time in T6 treatment. 1 – 140; 2 – 160; 3 – 180; 4 – 200; 5 – 220; 6 – 240 °C

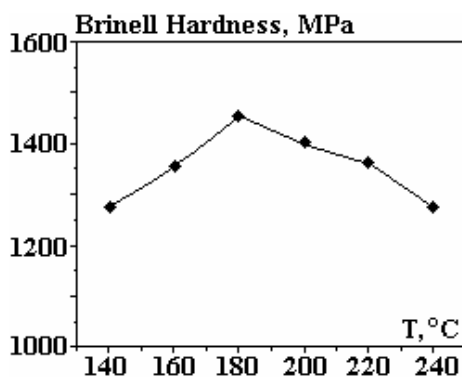


Fig. 2. Peak hardness variation with ageing temperature in T6 treatment

Fig. 3 shows the polarization curves for peak aged, over aged and under aged composite samples. It is clearly evident that the peak aged composites have a higher corrosion current and a lower corrosion potential. It can be stated that the peak aged is morphologically unstable in corrosion media since pitting corrosion dominates. The SEM observations clearly show that the peak aged composite is more prone to pitting corrosion (Fig. 4,a). This effect may arise due to the uniform distribution of precipitates of alloying elements during peak aging. Table 1 indicates that the polarization resistance for the peak aged composite is comparatively less and hence the corrosion rate is more. The peak aged composite is selected among the group of aged composites and the given cerium oxide coating obtained by chemical bath technique and further subjected to the electro chemical testing.

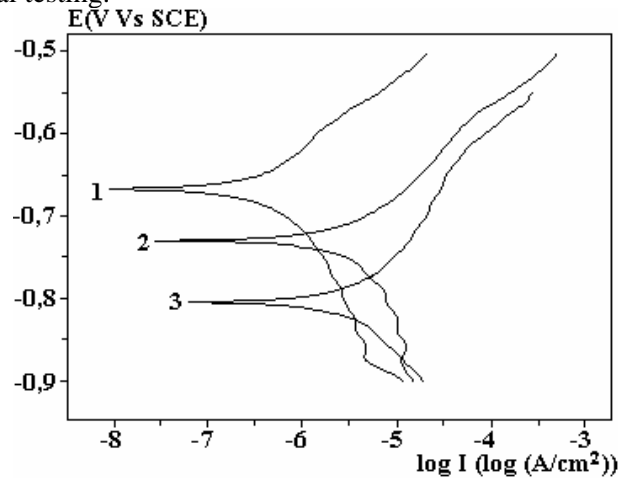


Fig. 3. Potentiodynamic polarization curves for the aged composites in 3.5N NaCl solution at 30 °C. 1 – over aged; 2 – under aged; 3 – peak aged

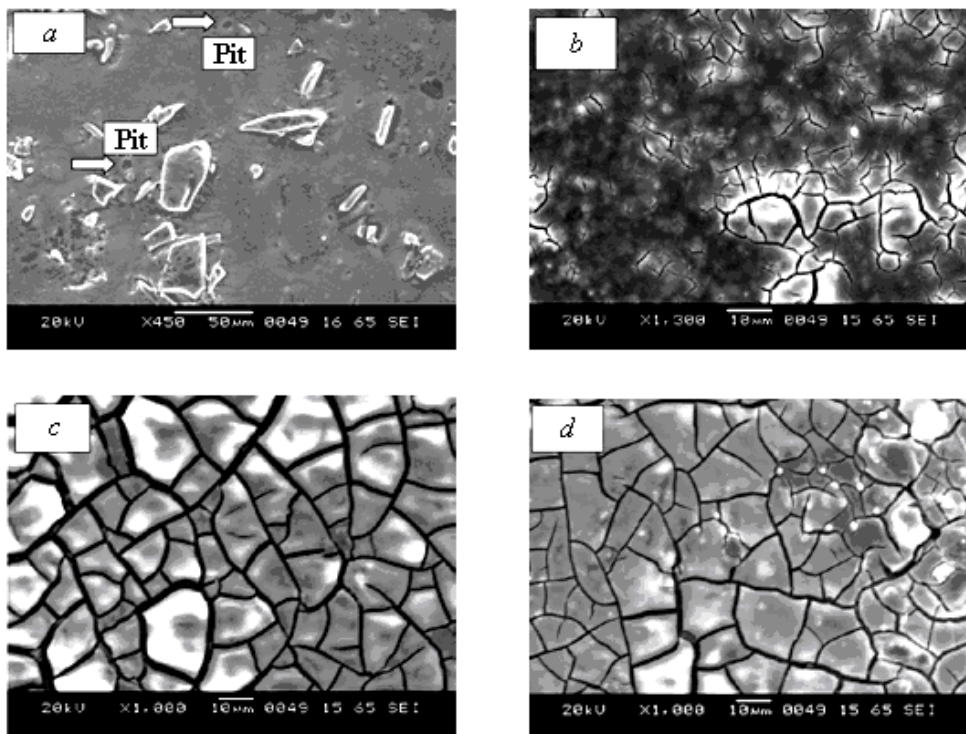


Fig. 4. (a) SEM microstructure of peak aged composite subjected to electro chemical testing Surface topography of different films after heat treatment at: (b) 300°C, (c) 400°C and (d) 500°C

Effect of heat treatment on the pitting corrosion behavior of the composite coated with cerium oxide

Highly uniform and ridge shaped crack bound cerium oxide films were deposited at different temperatures. But during the heat treatment the cracks widened and it affected the continuity of the film. The films heated at 300°C (Fig. 4,b) were characterized by non crystallized topography whereas the films heated at 400°C (Fig. 4,c) – by crystallized structure showing that cerium oxide crystallized between 300 and

400°C. Fig. 4,d clearly illustrates the highly uniform and crystallized structure of the films deposited at 500°C.

Table 1. Corrosion characteristics of aged composites in 3.5 N NaCl solution

Material's condition	Corrosion potential (E_{corr}) mV	Polarization resistance (R_p) $\text{K}\Omega/\text{cm}^2$	Corrosion current (I_{corr}) μA	Corrosion rate Mils/year
Over aged	-729	6.05	2.91	2.91
Under aged	-756	5.28	3.1	3.1
Peak aged	-804	3.99	3.65	3.65

Figure 5 illustrates the X-ray patterns of the CeO_2 films, in agreement with SEM observations. No peak was observed in the XRD patterns of the pyrolysed films (300°C), indicating that the pyrolysed films were amorphous. These films crystallized after heat treatments at or above 400°C, and the diffraction patterns of the films showed the presence of the crystalline cerianite phase of the face centered cubic CeO_2 oriented along the (111), (200), (220) and (311) planes.

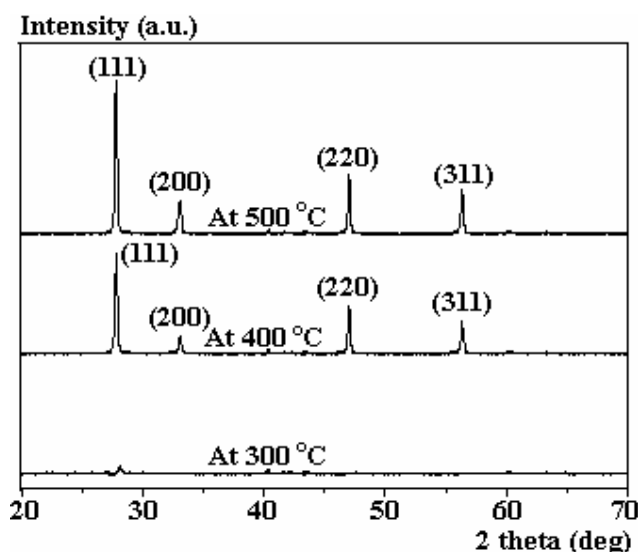


Fig. 5. XRD pattern of CeO_2 films heat treated at different temperatures

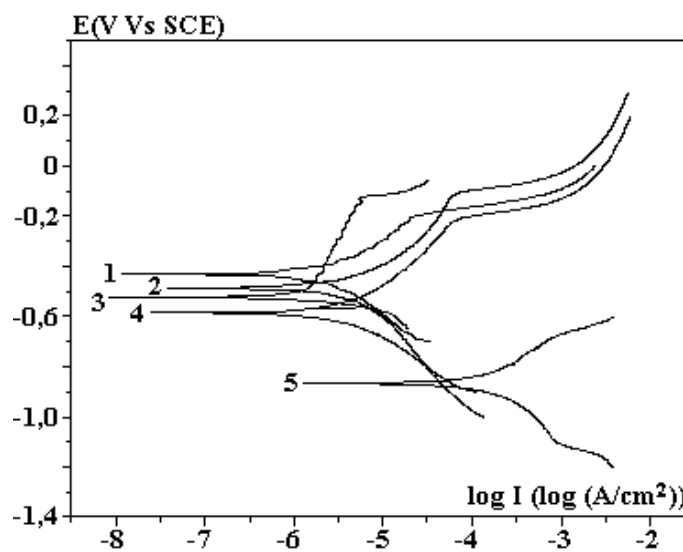


Fig. 6. Potentiodynamic polarization curves of the CeO_2 coated samples heat treated at different temperatures and the bare composite sample in 3.5 N NaCl solution. 1 – CeO coated; 2 – CeO coated and heat treated at 400 °C; 3 – CeO coated and heat treated at 300 °C; 4 – CeO coated and heat treated at 500 °C; 5 – peak aged specimen

The electrochemical behavior of the coated composite was studied by examining polarization curves obtained in 3.5 N NaCl aqueous solutions. Fig. 6 presents the polarization curves for the bare sample and CeO₂ coated samples subjected to heat treatment. It can be seen that the position of polarization curves for the CeO₂ coated composites shifts towards the positive direction. The coated samples have lower current density (I_{corr}), thus indicating that the CeO₂ coating improves the corrosion resistance of the composite to a large extent. This is evident by analyzing the pitting nucleation resistance (R) values of the CeO₂ coated composite samples. Table 1 shows the measured values of I_{corr} , E_{corr} , E_{pit} and $E_{\text{pit}}-E_{\text{corr}}$ indicating the pitting corrosion resistance of the films. The values of I_{corr} of the annealing coated samples at different temperatures was found to be less than those of the uncoated samples, especially for the annealing coatings at 300 °C. It means that the heat treatment at 300°C obviously improves the pitting corrosion resistance of the cerium oxide coating. In turn, the values of $E_{\text{pit}}-E_{\text{corr}}$ are observed to be more abrupt than those of other specimens with or without coating. It further proves that the excellent passive region ($E_{\text{pit}}-E_{\text{corr}}$) can be obtained for the cerium oxide coating heat treated at 300°C. As seen in Table 2, increased values of $E_{\text{pit}}-E_{\text{corr}}$ of the coated specimens in contrast to those of the uncoated samples indicate that the cerium oxide coatings can improve the pitting corrosion resistance of 6061 Al/SiC_p composite. From the results of the dynamic polarization scans it is clear that the pitting corrosion resistance of cerium oxide coating heat treated at 300°C is the best among the annealing coatings. It can be predicted that the improvement of the pitting corrosion resistance of cerium oxide coatings may correlate to the microstructure of cerium oxide obtained after heat treatment at 300 °C As seen in Figs. 1 and 2, when comparing the surface topographies and phases of the annealing coatings, the amorphous microstructure of the coatings after heat treatment is beneficial for improving their pitting corrosion resistance unlike the crystallized cerium oxide.

Table 2. Corrosion characteristics of the composite with and without CeO₂ coating

Material's condition	I_{corr} (μA)	E_{corr} (mV vs SCE)	E_{pit} (mV vs SCE)	$R = E_{\text{pit}} - E_{\text{corr}}$ (mV vs SSC)
Peak aged composite	3.65	-872	-735	137
CeO ₂ Coated	2.12	-416	-195	221
Heat treated at 300 °C	0.63	-546	-76	470
Heat treated at 400 °C	1.45	-588	-280	306
Heat treated at 500 °C	1.98	-440	213	227

Conclusions

- (1) Among the artificially aged composites (T6 treatment), the peak aged composite is more prone to pitting corrosion.
- (2) Cerium oxide coating by chemical bath technique increases the pitting nucleation resistance of 6061 Al/SiC_p composite.
- (3) The best corrosion resistance was obtained for the CeO₂ films heat-treated at 300°C; the cerium oxide films are of amorphous nature.
- (4) The widest passive region ($E_{\text{pit}}-E_{\text{corr}}$) was obtained for the CeO₂ films heat-treated at 300°C.

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Summary

One of the main drawbacks of 6061 Al/SiC_p is its poor pitting corrosion resistance in the aggressive environment containing chloride ions, such as seawater, for example. The present article deals with the investigations of effects of aging on the corrosion behavior of 6061 Al/SiC_p and of the heat treatment on the pitting corrosion resistance of 6061 Al/SiC_p coated by cerium oxide prepared by chemical bath technique. Potentiodynamic polarization test was used to study the corrosion behavior of cerium oxide coatings in 3.5N NaCl solution. The microstructure of cerium oxide was examined by scanning electron microscopy (SEM) and the formed phases were identified by X-ray diffraction (XRD). The pitting corrosion resistance of the cerium oxide coating was found to be improved after heat treatment at 300 °C for 30 min.
