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Enhanced Corrosion Resistance of SiC_p/ 2009 Al by Cerium and Lanthanum Conversion Treatment

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Abstract. The present study investigates the effect of lanthanide chlorides conversion coatings on the corrosion response of the 2009 Al alloy and SiC_p reinforced 2009 Al MMCs. Electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization studies showed that the localized corrosion resistance increased after treatments with solutions having various combinations of $CeCl_3.7H_2O$ and $LaCl_3.7H_2O$, with maximum increase noticed for 5000ppm $CeCl_3.7H_2O$. It was found that the protection degree effect obtained under similar coating conditions for 25 vol.% SiC_p/2009 Al was relatively higher than 15vol.% SiC_p/ 2009 Al MMC, but both of them were less than that of the unreinforced alloy. Scanning electron microscopy (SEM) accompanied with energy dispersive spectroscopy (EDS) analysis revealed the deposition of Ce and/ or La oxides/ hydroxides on cathodic intermetallics/ SiC_p and the existence of crevices at the SiC_p/ matrix interfaces. X-ray photoelectron spectroscopy (XPS) results indicated that Ce was incorporated as Ce^{3+} and Ce^{4+} species in the coatings.

Introduction

Discontinuously (SiC_p) reinforced Al matrix composites have emerged as potential materials for various engineering applications (i.e. aerospace, naval and automotive industries) due to their high strength to weight ratio, stiffness and modulus [1]. However, the addition of reinforcements increases the corrosion sensitivity of the composites. Chromates have been extensively used as inhibitors or applied as anticorrosive pretreatments for Al alloys. In recent years, these are going to replace by lanthanide conversion treatments, because lanthanide salts have low toxicity, economical competitive and ability to enhance corrosion resistance properties [2].

Previously [3,4], it was found that $CeCl_3.7H_2O$/ NaCl concentration, pH of conversion solution, treatment time and temperature of immersing solutions played a significant role in the production of coating with better corrosion resistance. In the present study, the effects of binary lanthanide conversion films formed over 2009 Al alloy and composites by thermal activation technique were investigated by potentiodynamic polarization and EIS. Further, the conversion film developed on the respective samples was characterized using SEM. EDS, and XPS.

Experimental

The samples of 2009 Al and composites reinforced with 15 and 25 vol.% SiC_p, in this study, were of 40 × 15 × 2mm in size. The nominal composition of the 2009 Al was as follows (wt.%): 3.2-4.4 Cu; 1.0-1.6 Mg; ≤0.25 Si; ≤0.07 Fe; ≤0.1 Zn; reminder Al.

Before being treated, the samples were polished to 1200# grit, ultrasonically cleaned using acetone for 5 min and washed with plenty of water. Then the samples were immersed in a bath containing 3.5% NaCl aqueous solution (pH 6) accompanied with different concentration ratios of $CeCl_3.7H_2O$ and $LaCl_3.7H_2O$ (5000ppm: 0ppm, 3750ppm: 1250ppm, 2500ppm: 2500ppm, 1250ppm: 3750ppm and 0ppm: 5000ppm respectively) at 45°C for 60min, rinsed with DI water and followed by drying at 100°C for 30 min.

The protection degree of lanthanide conversion coatings was evaluated on a CHI660A electrochemical work station using, a three electrode cell with a flat working electrode of 0.28cm^2 exposed surface area, a saturated calomel reference electrode and a platinum foil counter electrode. EIS measurements were conducted at corrosion potential (E_{corr}) over a frequency range of 10^4 Hz down to 10^{-2} Hz; and a sinusoidal potential perturbation of 10mV amplitude. The impedance data were analyzed by the ZsimpWin 3.10 EChem Software (Michigan, USA). While, potentiodynamic polarization curves were performed in the anodic direction from -1100mV/SCE at with a scan rate of 0.5mV/sec until the anodic corrosion current density reached 5mA/cm^2.

Further, the lanthanide conversion coatings were observed using Hitachi S-530 scanning electron microscope. The chemical composition and the valence states of the elements of the coating were analyzed by EDS spectrometer (Oxford, INCA) and X-ray photoelectron spectrometer (Thermo Fisher Scientific, USA) with a monochromatic Al K_α radiation.

Results and Discussion

Surface Analysis. Fig. 1a shows SEM image corresponding to samples of 15 vol.% SiC_p/ 2009 Al after treated for 60 min at 45°C in the solution of 3.5% NaCl and adding with 3750ppm $CeCl_3.7H_2O$ + 1250ppm $LaCl_3.7H_2O$, post-dried for 30min at 100°C. From figure a series of “islands” dispersed over the area of the coating surface can be distinguished. EDS analysis of the different zones indicated that Ce and La oxides/ hydroxides precipitated mainly over the cathodic intermetallics such as Al-Cu/ Al-Cu-Fe and some extent on the $SiC_{p.}$ On the other hand, the surface observation of composites revealed the existence of crevices at the matrix/ reinforcement interfaces.

XPS studies (Fig. 2) of the present materials after treatment with 5000ppm $CeCl_3.7H_2O$ revealed the existence of Ce and oxygen in the form of CeO_2/ Ce_2O_3, $Ce(OH)_3$/ $Ce(OH)_4$ and Al_2O_3 in the conversion layer. It was depicted that Ce^{3+} and Ce^{4+} both were present in film and, the existence of Ce^{4+} played vital role in improvement of corrosion resistance due to its auto-protection properties [5].

Electrochemical Measurements. The effects of lanthanide conversion films on the corrosion resistance of 2009 Al and MMCs in 3.5% NaCl were evaluated by EIS and potentiodynamic polarization curves. Fig. 3 shows the polarization diagram contrast for treated and untreated samples. From these curves, it can be obviously seen, the corrosion potential (E_{corr}) did not vary after treatment and pitting potential (E_{pit}) was found close to E_{corr}. However, the maximum leftward displacement of the polarization curves were attained for samples treated in conversion solution having 5000ppm $CeCl_3.7H_2O$. In this particular case, the corrosion current density (i_{corr}) for 15 vol.% and 25 vol.% SiC_p/ 2009 Al MMCs, decreased from 57.4 µA/ cm^2 and 89.1µA/ cm^2 to 0.56µA/ cm^2 and 0.38 µA/ cm^2, respectively. While, in case of 2009 Al these values reduced from 52.41µA/ cm^2 to 12×10^{-2}µ A/ cm^2.

Fig. 4 indicates the Bode magnitude plots obtained for the samples, treated by thermal activation in solutions having different concentrations of Ce and La chlorides, after 1hr immersing in 3.5% NaCl at 35°C. For reference, the curves corresponding to untreated samples are also included in the figure. By analyzing these curves with ZSimpWin program using the $R_s(Q_f(R_f(C_{dl}R_t)))$ model (discussed elsewhere) [6], an enhancement in corrosion resistance properties after lanthanide coatings can be noted from an increase in impedance $|Z|$, partly due to the formation of Al_2O_3 layer on the matrix and partly due to the reduction in activity in the zones surrounding the cathodic intermetallics as a result of precipitation of lanthanide oxides/

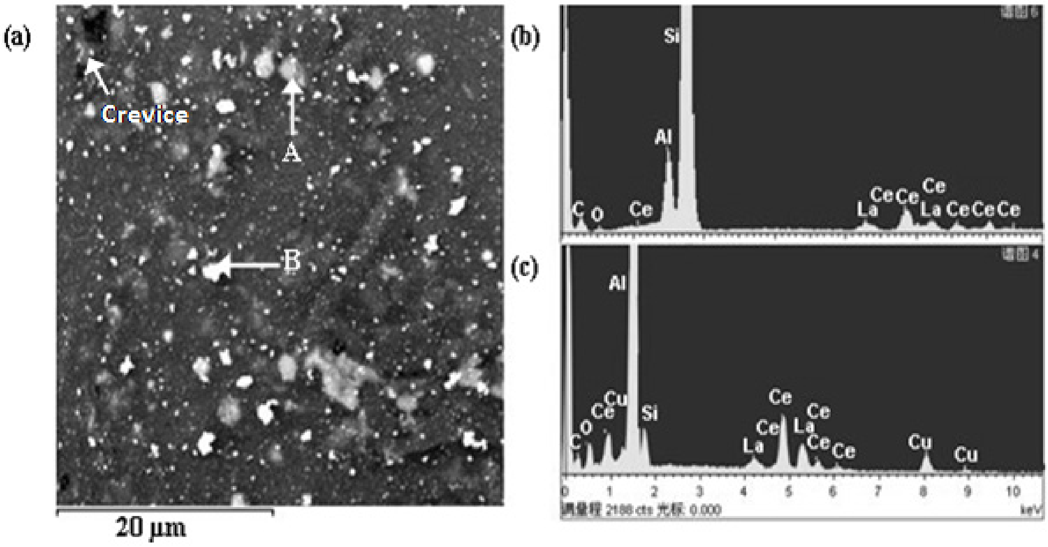

Fig. 1. (a) SEM image of lanthanide treated 15 vol.%SiC_p/2009 Al MMC; (b and c) EDS spectra acquired at points A and B, respectively.

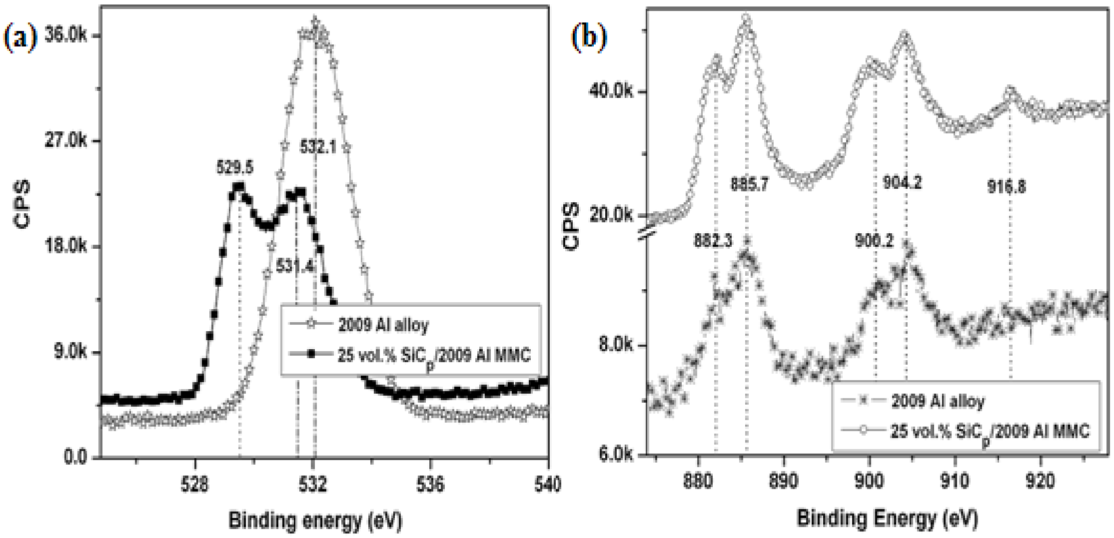

Fig. 2. XPS spectra obtained of lanthanide conversion coatings on 2009 Al and SiC_p/ 2009 Al MMC: (a) O 1s spectra; (b) Ce 3d spectra [4].

hydroxides. However, it can be observed that the polarization resistance (R_f+R_t) was only several kΩ-cm^2 for un-treated samples, while it was maximum increased to about 500 kΩ-cm^2 for 2009 Al and 300 kΩ-cm^2 for 15 vol.% SiC_p/ 2009 Al MMC after treating with 5000ppm $CeCl_3.7H_2O$+3.5% NaCl solution. A wide flattening of the maximum in the θ-log(f) curves were also noted for the samples treated under these particular conditions.

Further, the variation of percentage inhibition efficiency (IE, %) with $CeCl_3.7H_2O$ and $LaCl_3.7H_2O$ conversion coatings was calculated by using the following relation [6] :

$$\mathrm{IE}\,(\%) = \left(1 - R_{\mathrm{WO}}/R_{\mathrm{WI}}\right)\times 100 \tag{1}$$

Where, R_{WO} and R_{WI} are the total resistances (R_f +R_t), calculated from EIS, of as received samples and samples after lanthanide conversion treatment, respectively.

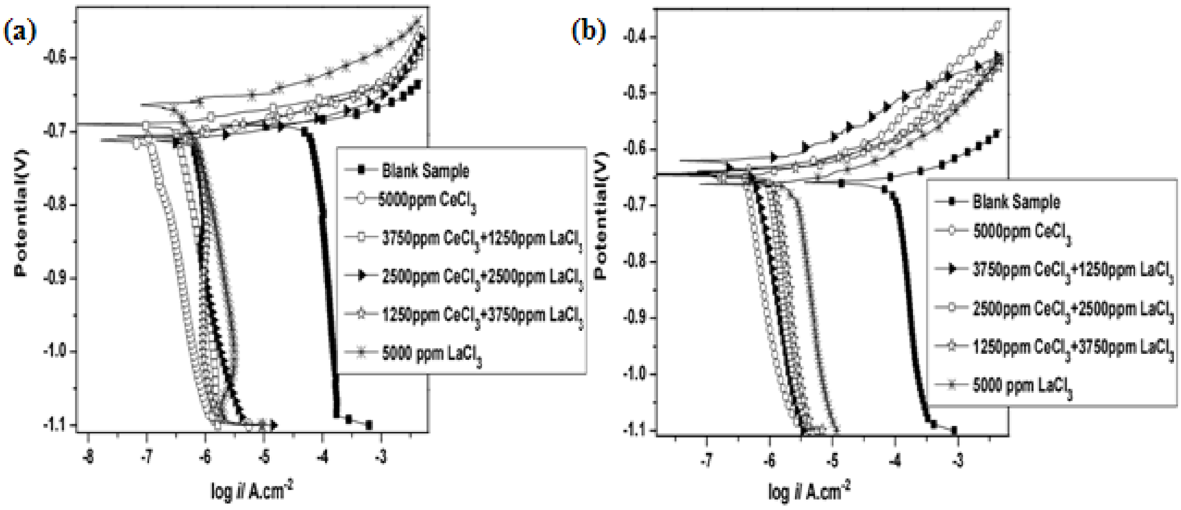

Fig. 3. Polarization curves acquired from untreated and lanthanide chloride treated; (a) 2009 Al alloy ;(b) 25 vol.% SiC_p/ 2009 Al MMC in 3.5% NaCl solution.

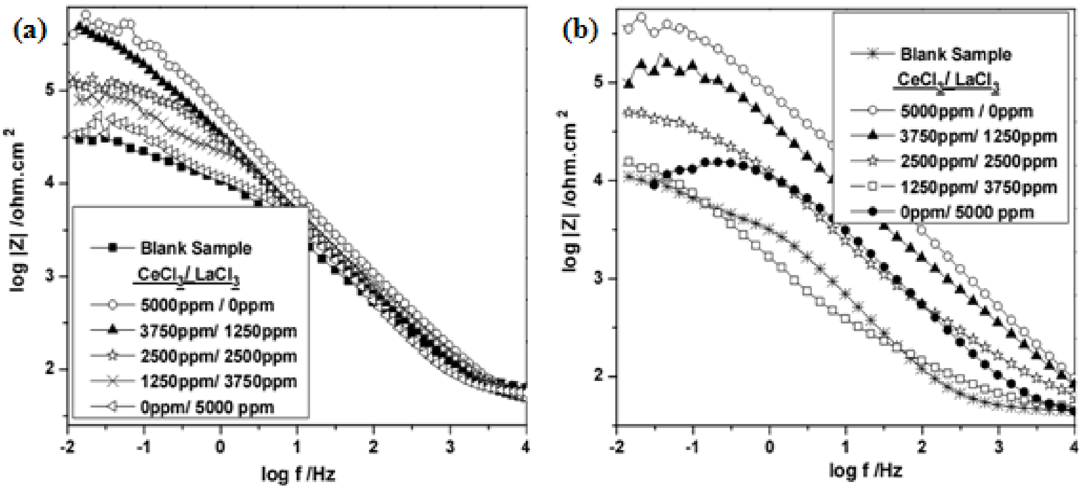

Fig. 4 Bode (amplitude vs. frequency) curves acquired from un-treated and lanthanide treated 2009 Al and 15 vol.% SiC_p/ 2009 Al MMC.

From Fig. 5, it can be observed that maximum inhibition efficiency was attained for samples treated with solutions having 5000ppm $CeCl_3.7H_2O$. While, similar to potentiodynamic polarization results, a relatively higher protection effect were noted for 2009 Al than SiC_p reinforced 2009 Al MMCs. These findings can be explained as, due to lower activity of lanthanides other than Ce to form lanthanide oxides/ hydroxides film on the cathodic side [7] and, as the existence of crevices at the matrix/ SiC_p interfaces.

Conclusions

The studies carried out by electrochemical and surface analysis techniques revealed that:

(i) Compared with the un-treated 2009 Al and MMCs, surface modification by $CeCl_3$ and $LaCl_3$ coatings resulted in increase of corrosion resistance, with maximum increase observed by 5000ppm $CeCl_3.7H_2O$.

(ii) The improved resistance offered by coatings was due to the decrease of both cathodic and anodic reaction rate as a result of sufficiently coverage of cathodic sites by lanthanide oxides/ hydroxides.

(iii) Relatively better protection achieved with Ce than La was due to the existence of Ce^{4+} species in coatings, which supplies auto protection to the film.

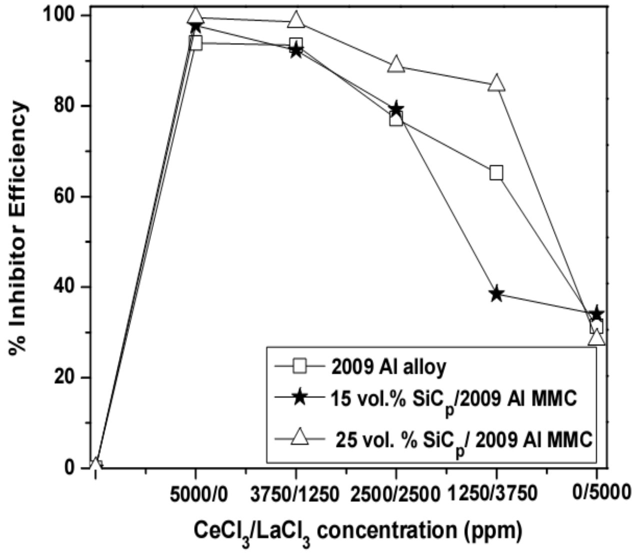

Fig. 5. Variation of inhibition efficiency (%) with $CeCl_3.7H_2O$ and $LaCl_3.7H_2O$ concentrations.

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