AUTHOR QUERY FORM

Journal: CS Article Number: 4327	Please e-mail or fax your responses and any corrections to: E-mail: corrections.esil@elsevier.sps.co.in Fax: +31 2048 52799
---	---	---

Dear Author,

Please check your proof carefully and mark all corrections at the appropriate place in the proof (e.g., by using on-screen annotation in the PDF file) or compile them in a separate list. To ensure fast publication of your paper please return your corrections within 48 hours.

For correction or revision of any artwork, please consult <http://www.elsevier.com/artworkinstructions>.

Any queries or remarks that have arisen during the processing of your manuscript are listed below and highlighted by flags in the proof. Click on the 'Q' link to go to the location in the proof.

Location in article	Query / Remark: click on the Q link to go Please insert your reply or correction at the corresponding line in the proof
Q1	Research highlights are 3–5 bullet points, no more than 85 characters per bullet point. Please provide it in correct format. For more information, see www.elsevier.com/researchhighlights .

Thank you for your assistance.

Research highlights

► We studied the corrosion resistance of Al/Al₃Ti and Al/Al₃Zr. Volume fraction of intermetallic platelets strongly influences the corrosion behaviour. Galvanic effects between platelets and the metallic matrix occur. A low segregation of platelets leads to an improvement of the corrosion behaviour. The FGM concept allows balancing between mechanical and corrosion properties.

Contents lists available at ScienceDirect

Corrosion Science

journal homepage: www.elsevier.com/locate/corsci

Corrosion behaviour of Al/Al₃Ti and Al/Al₃Zr functionally graded materials produced by centrifugal solid-particle method: Influence of the intermetallics volume fraction

S.C. Ferreira^a, L.A. Rocha^{a,*}, E. Ariza^a, P.D. Sequeira^a, Yoshimi Watanabe^b, J.C.S. Fernandes^c

^a Centre for Mechanical and Materials Technologies, Department of Mechanical Engineering, University of Minho, Campus de Azurém, 4800-058 Guimarães, Portugal

^b Department of Engineering Physics, Electronics and Mechanics, Graduate School of Engineering, Nagoya Institute of Technology, Gokiso-Chu, Showa-Ku, 466-8555 Nagoya, Japan

^c ICEMS/DEQB, Instituto Superior Técnico, TULisbon, 1049-001 Lisboa, Portugal

ARTICLE INFO

Article history:

Received 29 March 2010

Accepted 7 February 2011

Available online xxx

Keywords:

A. Aluminium

A. Intermetallics

B. EIS

B. SEM

C. Pitting corrosion

ABSTRACT

Intermetallic particles, Al₃Ti and Al₃Zr were formed in Al–5mass%Ti and Al–5mass%Zr alloys, respectively, by centrifugal casting, in order to create functionally graded materials (FGMs). At present, no information is available on the influence of the amount of intermetallics on the electrochemical properties of these alloys.

In this paper, the corrosion resistance of Al/Al₃Ti and Al/Al₃Zr FGMs was investigated by open-circuit measurements, potentiodynamic polarization and electrochemical impedance spectroscopy. Results suggest that the corrosion resistance of the FGMs is affected by galvanic effects between the intermetallic particles and the metallic matrix. Lower centrifugal forces resulted in an improvement of the electrochemical properties.

© 2011 Published by Elsevier Ltd.

1. Introduction

The corrosion behaviour of aluminium alloys has been the subject of a large number of publications, since the naturally formed oxide film can give excellent protection against corrosion, in addition to the advantages resulting from aluminium's low density [1]. Many commercial aluminium alloys are developed with a wide range of mechanical properties stimulated by careful alloying additions and heat-treatments [2]. According to the Al–Ti and Al–Zr phase diagrams, the intermetallic compounds of Al₃Ti and Al₃Zr are formed through crystallization as primary crystals [3]. Both compounds have similar crystal structures i.e., D0₂₂ in Al₃Ti and D0₂₃ in Al₃Zr with the same tetragonal space samples of 14/mmm and show high melting temperature, low density, good oxidation resistance and good thermal stability [4].

The corrosion resistance of the aluminium alloys is usually dependent on the metal heterogeneities and/or on the medium or exposure conditions. Heterogeneities in the microstructure can cause formation of cathodic and anodic zones that promote different forms of localised corrosion [2,5–8]. The production of local galvanic cells leads to the dissolution of the less noble areas [9]. In the case of the aluminium alloys, the heterogeneities are frequently intermetallic compounds distributed throughout the metallic matrix that can be either anodic or cathodic relatively to

the matrix. In the case of the Al₃Ti and Al₃Zr intermetallic compounds, they show a more cathodic potential in comparison with the pure aluminium (pure Al_[99,99] = –849 mV_{SCE}; Al₃Ti = –799 mV_{SCE} and Al₃Zr = –801 mV_{SCE} in 0.6 M NaCl solution) [2]. Consequently, depending on the environmental conditions, they are able of inducing localised corrosion in the metallic matrix surrounding the intermetallic compounds. Additionally, the presence of intermetallic compounds in the aluminium matrix can difficult the growth or promote failures of the protective oxide layer formed in air or in aqueous solutions on alloys that are likely to be passivated [2,5]. However the influence of the volume fraction of intermetallic compounds on the corrosion behaviour of these materials is still unknown.

Functionally graded materials (FGMs) are considered as engineered materials systems produced to achieve optimum performance in an intended application. FGMs are produced using techniques that introduce spatial differential distribution of the reinforcing along the component. As end result a gradient of mechanical properties from the surface up to the bulk of the components is obtained.

The Al/ceramics and Al/intermetallic compound particles FGMs can be fabricated by a centrifugal method [10–19]. The composition gradient is achieved primarily by the difference in the centrifugal force produced by the difference in density between the molten metal and particles. The fabrication of the intermetallic compounds dispersed FGMs made by the centrifugal method can be classified into two categories based on the liquidus temperature

* Corresponding author. Tel.: +351 253 510231; fax: +351 253 516007.

E-mail address: lrocha@dem.uminho.pt (L.A. Rocha).

of the master alloy [13–16,19]. One is the centrifugal solid-particle method, where the processing temperature is lower than the *liquidus* temperature of the master alloy, and the dispersed solid phase or particles in the master alloy are stable in a liquid matrix. On the other hand, if the processing temperature is superior than the *liquidus* temperature, a centrifugal force can be applied during the solidification both to the nucleated intermetallic compound and to the molten matrix. This method is named as a centrifugal *in situ* method. The processing conditions by centrifugal solid-particle method as well as the mechanical properties of Al/intermetallics compound FGMs, namely of the Al/Al₃Ti and Al/Al₃Zr systems, have been investigated [18].

In this paper, corrosion behaviour of the Al/Al₃Ti and Al/Al₃Zr FGMs in a 0.6 M NaCl has been studied in the outer region of the FGM rings manufactured by centrifugal solid-particle method, at where intermetallic compounds are condensed. For such, open-circuit potential, potentiodynamic **polarization** and electrochemical impedance spectroscopy (EIS) tests were carried out. The EIS spectra were modelled and analysed with an equivalent circuit that reflected the evolution of corrosion behaviour during 1, 3, 6 and 10 days of immersion.

2. Materials and methods

The Al/Al₃Ti and Al/Al₃Zr FGMs were produced by the centrifugal solid-particle method, from **Al-5mass%Ti** and **Al-5mass%Zr** commercial alloys, respectively, as described by Sequeira et al. [18]. Since the relative atomic masses of Al, Ti and Zr are 26.98, 47.88 and 91.22, respectively, the theoretical volume fraction of platelet particles of Al₃Ti in the master alloy was calculated to be approximately **11 vol.%** and that of Al₃Zr as approximately **7 vol.%** [18]. In the centrifugal solid-particle method, the alloy is heated up to a temperature located between its *solidus* (or invariant reactions) and *liquidus* temperatures, were most of the intermetallic compound platelets remain solid in a liquid Al-based matrix. It is then poured into a rotating mould in order to obtain ring-shaped samples which have an outer diameter of 90 mm, a height of 25 mm and a thickness of **20–25 mm** (Fig. 1). The temperature of the melting furnace was 1173 K and the applied centrifugal casting forces were 30, 60 and 120 G (units of gravity). Due to the density difference between intermetallic compounds and the master alloy, the FGM rings had compositional gradient in the radial direction where the outer region of the rings was richer in platelet particles.

The samples were polished metallographically using standard metallographic technique, ultrasonically cleaned in ethanol and in distilled water and finally dried.

The corrosion behaviour was evaluated on the outer region of the each sample by potentiodynamic polarization and EIS tests

(see Fig. 1). All electrochemical tests were performed at ambient temperature in a naturally aerated 0.6 M NaCl solution. The electrochemical cell consisted in a standard three electrode arrangement. The counter electrode was a platinum sheet with an area of 1 cm² and a saturated calomel electrode (SCE) was used as reference. The area of the working electrode was defined as 0.4 cm². A PGP201 Potentiostat/Galvanostat (Radiometer Denmark), controlled by the VoltaMaster-1 software, was used to carry out the polarization measurements, while a Voltalab PGZ100 Potentiostat (**radiometer analytical**), controlled by the VoltaMaster-4 software, was used for the EIS measurements. Prior to polarization test, the open-circuit potential (OCP) was monitored during 3600 s, after which the samples were polarized, in the anodic direction, from **–1400 to 200 mV** at a scan rate of **2 mV s^{–1}**. After the polarization test, the samples were examined using a scanning electron microscope (SEM). The EIS measurements were performed in the frequency range from 100 kHz to 5 MHz, with a sinusoidal signal of amplitude 10 mV rms applied to the electrode at its corrosion potential. EIS measurements were performed at increased immersion times of the 1, 3 and 6 and 10 days. For EIS data fitting, the ZView2 software was used.

3. Results and discussion

3.1. General considerations of gradient distribution of particles

Sequeira et al. [18] have presented a study where the particle distribution in Al/Al₃Ti and Al/Al₃Zr FGMs produced by the centrifugal method is evaluated by optical microscopy (OM). In this study, it was shown that higher applied centrifugal force increases both Al₃Ti and Al₃Zr intermetallic particles area fraction in the outer regions of the FGMs. Moreover, the increase of applied centrifugal force from 60 G to 120 G does not affect significantly the area fraction for the outermost region of the FGMs but does increase it for the adjacent regions (Fig. 2). Based in these results, the area fraction occupied by particles on the outer region of the FGM rings or region of the corrosion test was calculated and is present in Table 1. In fact, the area fraction of Al₃Ti at the surface of the samples is almost independent on the centrifugal force used for producing them. However, in the Al/Al₃Zr FGM samples, a clear increase in the area fraction with the raise in centrifugal force is observed.

3.2. Open-circuit potential and potentiodynamic polarization tests

After being immersed in the 0.6 M NaCl solution, the corrosion potential (E_{corr}) of the samples was monitored during 3600 s. The obtained curves are presented in Fig. 3. As it can be observed, all samples reveal an increase in the corrosion potential with the time, indicating, the growth of the passive film. The Al/Al₃Ti FGM samples show a similar behaviour, in terms of thermodynamic stability, regardless the processing conditions, with values of E_{corr} ranging between **–850 and –800 mV** (Fig. 3a). Conversely, the Al/Al₃Zr FGM samples present a more dispersed behaviour (Fig. 3b). The sample of 30 G reveals an E_{corr} clearly higher (**–825 mV**) than the 60 G and 120 G samples ($E_{\text{corr}} \sim \text{–950 mV}$), at the end of 3600 s. The more active corrosion potential exhibited by these two last samples reflects its less thermodynamic stability and therefore its higher corrosion tendency.

Fig. 4 presents the anodic **polarization** curves obtained for all samples. As it can be observed in Fig. 4a, the corrosion behaviour of Al/Al₃Ti FGM samples is very similar. However, in the case of the Al/Al₃Zr FGM samples, the samples obtained with 60 and 120 G, in accordance to the **open-circuit** potential results, appear to reveal the worst corrosion behaviour (Fig. 4b), exhibiting an

Fig. 1. Schematic drawing of the FGM ring indicating the position of the studied region.

Fig. 2. Intermetallic particles area fraction in: (a) Al/Al₃Ti FGMs and (b) Al/Al₃Zr FGMs. The outer of the ring is represented as the position 1.0 and the inner of the ring by position 0.0 of the normalized thickness.

Table 1
Area fraction occupied by platelets on the outer region of FGM rings.

Al/Al ₃ Ti FGMs (G)	Area fraction occupied by Al ₃ Ti	Al/Al ₃ Zr FGMs (G)	Area fraction occupied by Al ₃ Zr
30	0.169 ± 0.053	30	0.127 ± 0.002
60	0.162 ± 0.089	60	0.144 ± 0.073
120	0.168 ± 0.067	120	0.173 ± 0.011

lower $E_{(i=0)}$ potential. A passive plateau was never detected in any of the samples, indicating active corrosion of the materials. Also, as it can be observed in Fig. 4, the determination of the corrosion current density (i_{corr}) for all samples presents some difficulties because of the signal noise and instability of the samples immersed in the electrolyte.

Fig. 5 shows the surface morphology of the Al/Al₃Ti FGM 120 G sample before and after the polarization test. Before polarization, the sample presented some porosity (Fig. 5a), typical of a material processed by casting technologies that might have contributed to facilitate the penetration of the electrolyte in the material inducing corrosion. Also, the presence of this porosity introduces non-measurable errors on the calculation of the effective area of contact between the material and the solution. After the polarization test, the sample reveals a large degradation, especially in the nearby regions to the reinforcing particles. As it can be seen in Fig. 5b the Al₃Ti platelets are not attacked. Similar behaviour was obtained for the other Al/Al₃Ti FGM samples.

In the case of Al/Al₃Zr FGM 120 G sample, representative micrographs obtained by SEM observation are presented in Fig. 6. As it can be seen, the concentration of small and thin platelets in Al/Al₃Zr FGM samples appears to be higher than that found in Al/Al₃Ti FGM samples (compare Fig. 6a) with Fig. 5a. While, Al/Al₃Ti FGM 120 G present platelets with similar thickness, but with some variation on the longitudinal dimension, in the case of Al/Al₃Zr FGM 120 G, some thick and long platelets are observed together with those possessing smaller dimensions. As observed in Fig. 6b, Al/

Al₃Zr FGM 120 G samples suffered a high degradation in the neighbouring regions to the platelets, with morphology similar to that observed in the Al/Al₃Ti FGM samples, after the polarization test.

As indicated by the open-circuit potential and potentiodynamic polarization results, Al/Al₃Zr FGM samples obtained with 60 G and 120 G revealed a worst behaviour when compared with the Al/Al₃Zr obtained with 30 G. This phenomenon can be explained by the lower volume fraction of platelets found in the sample obtained with 30 G. In fact, as before mentioned, at high applied centrifugal forces, Al₃Zr particles have a higher segregation rate. Therefore we can presume that the degradation of FGMs material intensifies as the concentration of reinforcement platelets increase.

Biribilis et al. [2] refer that the corrosion resistance of aluminium alloys is influenced by the presence of intermetallic compound particles exhibiting different electrochemical characteristics from those of the matrix. When the intermetallic compound particles are more noble than the matrix, as it happens with Al₃Ti and Al₃Zr [20], circumferential pits appear as a circle of attack around a more or less intact particle. This type of morphology has been ascribed to localised galvanic attack of the more active matrix by the nobler particle.

According to Pardo et al. [21], pitting attack is reported to be the major form of corrosion in aluminium based metal matrix composites (MMCs). Preferentially, the attack occurs at the matrix/reinforcement interface. Furthermore, pores, second-phase particles and interfacial reaction products can all influence corrosion behaviour in a significant way. The addition of a reinforcing phase could lead to further discontinuities in the passive film, increasing the number of sites where corrosion can be initiated and rendering the composite liable to severe attack. On the other hand, more pits are formed on aluminium based MMCs than on unreinforced alloys.

In fact, for the systems under study in this work, the intermetallic compound platelets are noble when compared with the aluminium matrix and might act as cathodic regions, facilitating the dissolution of the protective passive film and conducting to a pref-

Fig. 3. Evolution of corrosion potential with time: (a) Al/Al₃Ti FGMs; (b) Al/Al₃Zr FGMs.

Fig. 4. Anodic polarization curves: (a) Al/Al₃Ti FGMs and (b) Al/Al₃Zr FGMs.

erential attack in the regions of the matrix near to the reinforcements. Thus, the higher degradation observed in the outer region of Al/Al₃Zr FGM samples (obtained with 60 G and 120 G) is explained by the higher concentration of particles (high cathodic to anodic ratio) in this region of the sample when compared with the Al/Al₃Zr FGM sample obtained with 30 G.

3.3. Electrochemical impedance spectroscopy and spectra modelling

Experimental EIS results from Al/Al₃Ti and Al/Al₃Zr FGMs after 1, 3, 6 and 10 days exposure to the 0.6 M NaCl solution are presented in the Bode plots in Figs. 7 and 8, respectively. An overall analysis of the spectra indicates the presence of an oxide film over the metallic matrix, which is responsible for a time constant at high frequencies. Moreover, a second time constant is evident at lower frequencies, probably due to localised corrosion processes, as it happens, for instance, in the case of pitting [22].

The surface of both materials is expected to be mostly covered by an oxide film, formed over the matrix. However, the presence of particles of Al₃Ti or Al₃Zr, both of them known to be more noble than the aluminium matrix [20], as mentioned above, will lead to localised galvanic corrosion of the surrounding matrix, as shown in the schematic illustration of Fig. 9.

The equivalent circuit depicted in Fig. 10 was proposed to describe the behaviour of this kind of materials. The components of these equivalent circuits are: R_e , ohmic resistance of the electrolyte, the loop $R_{ox}-C_{ox}$, respectively, the resistance and capacitance

of the oxide layer, and the contribution of the processes taking place at the particles: the $R_{ct}-C_{dl}$ network that represents the charge transfer reaction corresponding to localised corrosion and the capacitance of the double layer, added to the additional resistance of the electrolyte inside the pore. As R_{ox} tends to be extremely high, not allowing for any conduction of electrons inside the oxide film, this circuit element is usually removed from the equivalent circuit, that transforms into the one depicted in Fig. 11.

Table 2 shows the parameters of fitting results. The values of both the resistances R'_e and R_{ct} are always higher for the Al/Al₃Ti FGM samples than for the Al/Al₃Zr FGM samples, which may be considered as an indication of the superior corrosion performance of Al/Al₃Ti FGMs.

The values of R'_e are dependent on the area occupied by the cavities resulting from the galvanic corrosion of the matrix in the vicinity of the intermetallic particles. Thus, R'_e should mainly depend on the area fraction of these particles. In fact R'_e values are almost constant (at the same immersion time) for the different types of Al/Al₃Ti FGMs, in accordance with Table 1, where the area fraction occupied by Al/Al₃Ti platelets on the outer region of FGM rings is shown to be nearly independent from the centrifugal force applied. In the case of Al/Al₃Zr FGMs, the values of R'_e decrease with increasing centrifugal force, as expected from Table 1, where the area fraction occupied by Al/Al₃Zr platelets on the outer region of FGM rings continuously increases from 30 G to 120 G.

The evolution of R'_e values with immersion time is also quite different for the two types of FGMs. In fact, R'_e is almost constant for

Fig. 5. SEM micrographs obtained on Al/Al₃Ti FGMs 120 G: (a) before polarization and (b) after polarization test in 0.6 M NaCl solution.

Fig. 6. SEM micrographs obtained on Al/Al₃Zr FGMs 120 G: (a) before polarization and (b) after polarization test in 0.6 M NaCl solution.

the Al/Al₃Ti FGMs, whereas for the Al/Al₃Zr FGMs a clear decrease with time is noticed. This behaviour may be interpreted in terms of the relative stability of both materials, once more indicating that the Al/Al₃Ti FGMs should be more corrosion resistant than Al/Al₃Zr FGMs.

As the oxide layer is formed over the Al matrix, the film capacitance, C_{ox} , was expected to behave similarly for both types of FGMs. However, this was not the case, and, in particular, its different evolution with the immersion time may also be used as an indication of the corrosion performance of the different materials. It may be noticed that the values obtained immediately after immersion for the Al/Al₃Ti FGMs are generally higher than the ones obtained for the Al/Al₃Zr FGMs. Moreover, no significant differences were noticed in the values obtained, at similar immersion times, for the samples prepared with different centrifugal forces. Finally, a tendency for an increase of the capacitance values with immersion time was found. Two different reasons may explain this tendency. First of all, it may be accepted that, once the corrosion attack starts, the corroded areas may become covered by a new oxide film, increasing the real surface area occupied by the film and, thus, the measured capacitance values. Other explanation may be related to the hydration of the oxide film upon immersion. In fact, according to the expression for the capacitance:

$$C = \epsilon_0 \epsilon \frac{S}{d} \quad (1)$$

where ϵ_0 is the vacuum permittivity, the capacitance is dependent on the dielectric constant of the oxide film, ϵ , on the sample surface area, S ; and on the thickness of the film, d . Assuming that the surface area of the oxide does not change significantly upon immersion

and that the same applies to the oxide thickness, the continuous increase of the capacitance values may only be explained on the basis of the change of the dielectric constant. In fact, ϵ is known to range from 9, in the case of a dry oxide, to 40, for a partially hydrated layer [23]. The tendency for capacitance rise may then be linked with increasing hydration and, thus, to decreasing corrosion performance of the materials. Comparing the different samples, it may be noticed that the ratio of capacitance values obtained for 1d and for 10d of immersion is much lower for the Al/Al₃Ti FGMs (1.5, 1.2 and 1.07, respectively, for samples prepared at 30 G, 60 G and 120 G) than for the Al/Al₃Zr FGMs (2.35, 3.9 and 3.5, respectively, for samples prepared at 30 G, 60 G and 120 G). This may be considered an indication of the superior corrosion performance of Al/Al₃Ti FGMs.

Finally, the analysis of R_{ct} values shows a tendency towards lower values as the immersion time increases. This may be explained on the basis of an increase of the real area where the corrosion processes are taking place. Although the geometrical surface area of the samples (used to divide the impedance and, thus, the resistance values) is kept constant, the evolution of the corrosion process occurring in the contact between the matrix and the platelets will result in larger corroded zones (cf. Fig. 9) and, thus, increasing active areas. In accordance with the open-circuit potential and the potentiodynamic polarization results, which showed a little better corrosion behaviour for Al/Al₃Ti 60 G samples (Figs. 3a and 4a), these samples show the highest R_{ct} values for longer immersion times and also the highest R'_e values, confirming its better corrosion performance.

On the other hand, the Al/Al₃Zr FGM samples present a sharper decrease in the R'_e and R_{ct} values from 1 to 10 immersion days, indicating a more severe degradation of the material, as confirmed in the micrographs of Fig. 6. This phenomenon is corroborated by

Fig. 7. Bode plots of EIS spectra of Al/Al₃Ti exposed to 0.6 M NaCl solution: (a) 1 day; (b) 3 days; (c) 6 days and (d) 10 days.

Fig. 8. Bode plots of EIS spectra of Al/Al₃Zr exposed to 0.6 M NaCl solution: (a) 1 day; (b) 3 days; (c) 6 days and (d) 10 days.

the faster increase of the C_{ox} values with the immersion time in all Al/Al₃Zr FGM samples, as mentioned above. The lowest C_{ox} values

found in 30 G samples is an indication of the best corrosion behaviour of this type of sample among the overall Al/Al₃Zr FGMs, as

Fig. 9. Schematic representation of localized corrosion in the metal/intermetallics/oxide system.

Fig. 10. Schematic representation of localized corrosion and the proposed equivalent circuit.

Fig. 11. Equivalent circuit used for fitting the experimental data.

Although the presence of intermetallic compound particles in commercial **aluminium** alloys is widely used by foundry industries to produce components with good mechanical properties, the corrosion resistance can be significantly affected. When a compromise between good corrosion resistance and good mechanical properties is essential, an adequate volume fraction of particles in the composite must be estimated in order to not damage the performance of the material. Furthermore, the manufacturing of an FGM by centrifugal method can be useful for many applications. The role of FGM is expected to overcome the shortcomings of homogeneous composites, in which the gradation of properties is not present. FGMs exhibit a composition and/or microstructure variation in one specific direction, i.e., one surface with low volume fraction of intermetallic compound particles where corrosion resistance is required and another surface with high volume fraction of intermetallic compound particles where a mechanical property is required.

4. Conclusions

In the present study, influence of the amount of intermetallic platelets on the corrosion behaviour of Al/Al₃Ti and Al/Al₃Zr FGMs, when immersed in 0.6 M NaCl solution, at different immersion

Table 2

Parameters of the EIS of Al/Al₃Ti FGMs and Al/Al₃Zr FGMs.

Samples	Time (days)	R_e (Ω cm ²)	C_{ox} (μ F cm ⁻²)	R'_e (k Ω cm ²)	C_{dl} (μ F cm ⁻²)	R_{ct} (k Ω cm ²)
Al/Al ₃ Ti	30 G	1	10.54	66.55	10.89	1634
		3	10.58	67.06	9.53	832
		6	11.25	84.35	11.03	1688
		10	11.09	99.82	11.64	4094
	60 G	1	9.78	47.73	12.76	1259
		3	10.03	54.71	13.79	1584
		6	10.53	52.72	14.16	1775
		10	9.80	61.40	13.70	1587
	120 G	1	10.98	64.96	8.49	2296
		3	10.81	64.09	9.30	1941
		6	10.69	61.99	11.19	1907
		10	10.55	70.22	11.37	2394
Al/Al ₃ Zr	30 G	1	11.78	28.13	8.97	986
		3	11.87	31.27	7.52	2187
		6	12.30	47.74	5.68	2250
		10	11.69	65.80	4.30	2071
	60 G	1	10.92	26.66	7.35	696
		3	11.57	47.95	5.79	1405
		6	11.75	77.35	4.96	745
		10	11.43	107	4.74	1565
	120 G	1	11.62	27.63	6.58	781
		3	10.84	47.81	4.98	1035
		6	11.56	75.71	4.08	1136
		10	11.77	97.32	3.76	1841

times (1, 3, 6 and 10 days) was investigated. The results obtained are summarized as follows:

- (1) The electrochemical behaviour of FGM samples showed that galvanic effects between the intermetallic compound particles and the metal matrix affect the overall corrosion resistance of FGMs.
- (2) In case of Al/Al₃Ti FGM samples, the samples obtained with 60 G present the better corrosion resistance. In case of Al/Al₃Zr FGM samples, sample obtained with 30 G revealed better behaviour when compared with the obtained with 60 G and 120 G.
- (3) In general terms this behaviour can be associated to the particles segregation level, i.e., when a low segregation of particles is found in the material, associated to low applied centrifugal forces, the corrosion resistance of FGM appear to increase.
- (4) Trade-off properties of corrosion resistance and mechanical property can be achieved within the same specimen by using the FGM concept.

Acknowledgements

One of the authors (Y.W.) gratefully acknowledges the financial support provided by “Tokai Region Nanotechnology Manufacturing Cluster in *Knowledge Cluster Initiative*” by the Ministry of Education, Culture, Sports, Science and Technology of Japan. Acknowledgments also to “FCT”, Portugal, through the Project SFRH/BPD/5518/2001.

References

- [1] G.C. Caridade, M.I.S. Pereira, C.M.A. Brett, Electrochemical noise and impedance study of aluminium in weakly acid chloride, *Electrochim. Acta* 49 (2004) 785–793.
- [2] N. Birbilis, R.G. Buchheit, An experimental survey of electrochemical characteristics for intermetallic phases in aluminum alloys, *J. Electrochem. Soc.* 152 (2005) 140–151.
- [3] M.V. Karpets, Y.V. Milman, O.M. Barabash, N.P. Korzhova, O.N. Senkov, D.B. Miracle, T.N. Legkaya, I.V. Voskoboinik, The influence of Zr alloying on the structure and properties of Al₃Ti, *Intermetallics* 11 (2003) 241–249.
- [4] K.I. Moon, S.C. Kim, K.S. Lee, A study on the microstructure of D0₂₃ Al₃Zr and L1₂ (Al+12.5 at%Cu)₃Zr intermetallic compounds synthesized by PBM and SPS, *Intermetallics* 10 (2002) 185–194.
- [5] A. Aballe, M. Bethencourt, F.J. Botana, M.J. Cano, M. Marcos, Influence of the cathodic intermetallics distribution on the reproducibility of the electrochemical measurements on AA5083 alloy in NaCl solutions, *Corros. Sci.* 45 (2003) 161–180.
- [6] Z.S. Smialowska, Pitting corrosion of aluminum, *Corros. Sci.* 41 (1999) 1743–1767.
- [7] S.L. Winkler, M.P. Ryan, H.M. Flower, Pitting corrosion in cast 7XXX aluminium alloys and fibre reinforced MMCs, *Corros. Sci.* 46 (2004) 893–902.
- [8] V.I. Pokhmurs'kyi, L. Kwiatkowski, I.M. Zin', S.B. Lyon, L.M. Bilyi, M.B. Ratushna, Corrosion protection of aluminum alloys by inhibiting pigments, *Mater. Sci.* 42 (2006) 573–578.
- [9] A. Barbucci, G. Bruzzone, M. Delucchi, M. Panizza, G. Cerisola, Breakdown of passivity of aluminium alloys by intermetallic phases in neutral chloride solution, *Intermetallics* 8 (2000) 305–312.
- [10] Y. Fukui, Fundamental investigation of functionally gradient materials manufacturing system using centrifugal force, *JSME Int. J. Ser. III* 34 (1991) 144–148.
- [11] Y. Watanabe, N. Yamanaka, Y. Fukui, Orientation of Al₃Ti platelets in Al–Al₃Ti functionally graded material manufactured by centrifugal method, *Z. Metallkd.* 88 (1997) 717–721.
- [12] Y. Watanabe, N. Yamanaka, Y. Fukui, Wear behavior of Al–Al₃Ti composite manufactured by a centrifugal method, *Metall. Mater. Trans. A* 30 (1999) 3253–3261.
- [13] Y. Watanabe, Y. Fukui, Microstructures and mechanical properties of functionally graded materials fabricated by a centrifugal method, *Recent Res. Dev. Metall. Mater. Sci.* 4 (2000) 51–93.
- [14] Y. Watanabe, Y. Fukui, Fabrication of functionally-graded aluminum materials by the centrifugal method, *Aluminum Trans.* 2 (2000) 195–208.
- [15] Y. Watanabe, T. Nakamura, Microstructures and wear resistances of hybrid Al–(Al₃Ti+Al₃Ni) FGMs fabricated by a centrifugal method, *Intermetallics* 9 (2001) 33–43.
- [16] Y. Watanabe, H. Eryu, K. Matsuura, Evaluation of three-dimensional orientation of Al₃Ti platelet in Al-based functionally graded materials fabricated by a centrifugal casting technique, *Acta Mater.* 49 (2001) 775–783.
- [17] Y. Watanabe, A. Kawamoto, K. Matsuura, Particle size distributions in functionally graded materials fabricated by the centrifugal solid-particle method, *Compos. Sci. Technol.* 62 (2002) 881–888.
- [18] P.D. Sequeira, Y. Watanabe, L.A. Rocha, Particle distribution and orientation in Al/Al₃Zr and Al/Al₃Ti FGMs produced by the centrifugal method, *Mater. Sci. Forum* 492–493 (2005) 609–614.
- [19] P.D. Sequeira, Y. Watanabe, L.A. Rocha, Aluminium matrix texture and particle characterization in Al/Al₃Ti FGMs produced by a centrifugal solid-particle method, *Solid State Phenom.* 105 (2005) 415–420.
- [20] J.R. Scully, T.O. Knight, R.G. Buchheit, D.E. Peebles, Electrochemical characteristics of the Al₂Cu, Al₃Ta and Al₃Zr intermetallic phases and their relevancy to the localized corrosion of Al alloys, *Corros. Sci.* 35 (1993) 185–195.
- [21] A. Pardo, M.C. Merino, S. Merino, F. Viejo, M. Carboneras, R. Arrabal, Influence of reinforcement proportion and matrix composition on pitting corrosion behaviour of cast aluminium matrix composites (A3xx.x/SiCp), *Corros. Sci.* 47 (2005) 1750–1764.
- [22] F. Mansfeld, S. Lin, S. Kim, H. Shih, Pitting and passivation of Al alloys and Al-based metal matrix composites, *J. Electrochem. Soc.* 137 (1990) 78–82.
- [23] F.J. Martin, G.T. Cheek, W.E. O'Grady, P.M. Natishan, Impedance studies of the passive film on aluminium, *Corros. Sci.* 47 (2005) 3187–3201.