Corrosion Behavior of Ψ and β Quasicrystalline Al–Cu–Fe Alloy

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Abstract Two nanostructured Al–Cu–Fe alloys, $\text{Al}_{64}\text{Cu}_{24}\text{Fe}_{12}$ and $\text{Al}_{62.5}\text{Cu}_{25.2}\text{Fe}_{12.3}$, have been studied. Icosahedral quasicrystalline (ψ) $\text{Al}_{64}\text{Cu}_{24}\text{Fe}_{12}$ and crystalline cubic (β) $\text{Al}_{62.5}\text{Cu}_{25.2}\text{Fe}_{12.3}$ cylindrical ingots were first produced using normal casting techniques. High-energy mechanical milling was then conducted to obtain ψ icosahedral and β intermetallic nanostructured powders. Electrochemical impedance spectroscopy, linear polarization resistance, and potentiodynamic polarization were used to investigate the electrochemical corrosion characteristics of the powders in solutions with different pH values. Current density (i_{corr}), polarization resistance (R_p), and impedance modulus ($|Z|$) were determined. The results showed that regardless of pH value, increasing the solution temperature enhanced the corrosion resistance of the both phases. However, the electrochemical behavior of the ψ phase indicated that its stability depends on the submerged exposure time in neutral and alkaline environments. This behavior was related to the type of corrosion products present on the surfaces of the particles along with the diffusion and charge-transfer mechanisms of the corrosion process.

KEY WORDS: Nano-quasicrystalline; Al–Cu–Fe alloy; Mechanical alloying; Corrosion

1 Introduction

Quasicrystals present interesting properties such as low coefficients of friction and thermal conductivity, unusual optical properties, oxidation resistance, biocompatibility,

high hardness, and low electrical conductivity [1]. Only a small number of the potential applications of quasicrystalline materials have been commercialized after their discovery by Shechtman in 1984 [2]. This type of material represents a new challenge for material scientists and engineers. Today, quasicrystalline phases are encountered in over 100 alloy systems, of which the majority are aluminum based [1]. The alloying elements used to form aluminum-based quasicrystals are readily available, nontoxic, and reasonably priced. In addition to being interesting subjects for theoretical study, their complex atomic structures make these quasicrystals appealing for many practical purposes [1, 3]. Quasicrystals are promising as a reinforcing phase in composite materials; they have been suggested as filling phases for Al matrices and as reinforcing phases in maraging steels (yield stress of approximately 3 GPa) for surgical applications [4]. Recently, Al–Cu–Fe quasicrystals were suggested as fillers for ultra-high molecular weight polyethylene for use in acetabular cup prostheses [4]. Quasicrystals also have many useful properties that can be

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utilized in manufactured products such as thin films, coatings, and powder metallurgy for composite reinforcement. Many investigations have been conducted to improve composite performance by enhancing both physical and mechanical properties along with fabrication methods [3–11]. However, little information has been reported about the electrochemical corrosion behavior of nano-quasicrystalline powder phases because of the lack of an evaluation method or technique. The objective of this study is to evaluate the corrosion performance of ψ and β phases in alkaline, neutral, and acidic media.

2 Experimental

Aqueous solutions with different pH values (3, 7, and 11) were used as reference standards to conduct potentiodynamic polarization measurements following ASTM G 59-97 [12]. Furthermore, a standard reference test method for potentiostatic and potentiodynamic anodic polarization measurements (ASTM G 5-94 [13]) and the standard practice for algorithm verification and electrochemical impedance measurements (ASTM G 106-89 [14]) were used. The measurements were performed by applying conventional electrochemical techniques for corrosion monitoring with some variations (a nonconventional experimental setup) to allow the study of nano-quasicrystalline phases. Two alloy compositions of intermetallic Al–Cu–Fe nanoparticles were produced using analytic grade reagents (Al, Cu, and Fe with purity of 99.99%). First, normal casting techniques using SiC crucibles in the form of cylindrical ingots were employed. High-energy mechanical milling (HEMM) was conducted to obtain Al–Cu–Fe nanoparticle powders; the resulting compositions of the Ψ and β phases were $\text{Al}_{64}\text{Cu}_{24}\text{Fe}_{12}$ and $\text{Al}_{62.5}\text{Cu}_{25.2}\text{Fe}_{12.3}$ (at.%), respectively. Nanosized intermetallic and quasicrystalline powders were produced according to the procedure reported by Rosas *et al.* [15]. The electrochemical cell setup used for EIS, LPR, and PP experiments consisted of a saturated calomel electrode (SCE) as an electrode reference, a platinum wire as a working electrode, and a graphite auxiliary electrode. The electrodes were connected to a Gill AC (ACM instruments) potentiostat controlled by a personal desktop computer. Test solutions were prepared with analytical grade sodium hydroxide and sulfuric acid and distilled water. The pH values of the test solutions were adjusted to 3, 7, or 11 prior to each test. The pH measurements were made with an Oakton digital pH meter that had been previously calibrated. In all tests, 0.125 g of the ψ - and β -phase nanosized powders was suspended in 30 mL of the aqueous test solution. The suspended nanoparticles were expected to remain attached to the platinum electrode during the electrochemical tests. During each test, the temperature effects were evaluated,

and the solution was agitated in the turbulent regime. Electrochemical tests were conducted at 27 and 60 °C for periods of 80–120 h. To confirm the phase composition, the microstructural characteristics of the Ψ and β phases were characterized using high-resolution electron microscopy (HRTEM) measurements and X-ray diffraction (XRD). For the EIS tests, the AC Gill potentiostat was calibrated according to the ASTM G106-89 Standard. The EIS test conditions were as follows: AC current signal with an amplitude of 32 mV at open-circuit potential (OCP) in a frequency range of 30,000–0.01 Hz. The EIS data were recorded every 2 h, and the $|Z|$ impedance modulus was determined by monitoring the corrosion behavior. The LPR tests were conducted every 16 h between -100 and $+100$ mV according to the recommendations of the ASTM G 59-97 Standard. In addition, polarization curves were constructed using a sweep rate of 60 mV/min.

3 Results and Discussion

3.1 HEMM Powder Microstructures

The XRD patterns of the milled powders in Fig. 1a, b, respectively, confirm the presence of the Ψ and β phases before and after ball milling. The cubic β -phase is a BCC solid solution with an atomic composition of $\text{Al}_5(\text{Cu},\text{Fe})_5$. Figure 2 shows the respective HRTEM images in which the atomic planes of the ψ icosahedral quasicrystalline and β crystalline phases can be seen after ball milling.

3.2 Electrochemical Tests

Figure 3 shows the impedance modulus $|Z|$ for the ψ and β phases immersed in the different solutions at room temperature as a function of time. During the first 30 h of the test (first stage), $|Z|$ changes considerably, reaching maximum and minimum values oscillating between 2 and 37 Ω . For the first stage, the Nyquist diagram (Fig. 4) shows a straight line at 45°, indicating diffusion corrosion mechanisms.

After 30 h of testing (second stage), the variation in the $|Z|$ values decreases, indicating more homogeneous behavior for both phases with values between 2 and 15 Ω . However, in the second stage, the ψ phases in the solutions at pH values of 7 and 3 present the highest and lowest $|Z|$ values, respectively, and a large variance in $|Z|$ value is observed. In the second stage for solutions at all tested pH values, the principal corrosion mechanism was charge transfer, as indicated by the formation of a semicircle in the Nyquist diagram (Fig. 4). This behavior reveals the existence of barriers or films between the particle surfaces and the test solutions.

The impedance results coincide with the corresponding polarization curves shown in Fig. 5a. In this figure, the

Fig. 1 XRD patterns showing the presence of nanostructured ψ -phase **a**; β -phase **b** powders

Fig. 2 HRTEM images of nanostructured materials: **a** icosahedral quasicrystalline phase; **b** β crystalline phase

Fig. 3 $|Z|$ values versus time for the β and ψ nanostructured phases at room temperature and different pH values

anodic slope of the first-stage corrosion behavior for the two phases was asymptotic, reflecting continuous dissolution. In the second stage (after testing for 30 h), the anodic

Fig. 4 Nyquist diagram for β and ψ nanostructured phases at room temperature and different pH values

slope in the polarization curve presents a passivity region ranging from 500 to 800 mV_{SCE}. However, the passivity zone in the same curve is not completely homogeneous,

indicating a breaking and reformation cycle of the passive layer. This means that an ionic interchange process was responsible for the corrosion of the particles. A Pourbaix diagram for aluminum was used to explain the corrosion behaviors of the powders. The polarization curves shown in Fig. 5 indicate E_{corr} of 341–390 mV_{SCE} at room temperature and 60 °C for both phases. The Pourbaix diagram indicates that a bayerite ($\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$) layer can be formed.

The ($\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$) layer is not completely protective due to its high solubility. Furthermore, the bayerite dissolution could reduce the pH value of the solution [16]. This fact was confirmed by the results of the pH measurements obtained directly from the test solution at room temperature and 60 °C (Table 1). After 4 days of testing, the pH value of the solution tends to decrease for both phases. Thus, the randomness in the $|Z|$ values during the early stages of the corrosion test will depend on the variation in R_p . This might be attributed to the formation and dissolution of the oxide nonprotective layer, as indicated by the room temperature plot of R_p behavior, as shown in Fig. 6.

Pinheiro *et al.* [17] studied corrosion of $\text{Al}_{63.4 \pm 0.4}\text{Cu}_{24.0 \pm 0.9}\text{Fe}_{12.6 \pm 0.5}$ and $\text{Al}_{65.7}\text{Cu}_{22.2}\text{Fe}_{12.1}$ alloys using X-ray photoelectron spectroscopy and Auger electron spectroscopy. The Al signals increased, whereas those of Cu and Fe decreased when the ψ phase was in contact with oxidative environments. This trend is amplified when the quasicrystal phase is in contact with more severe environments. Based on our experimental results, the behavior reported by Pinheiro is consistent with the oxide layer composition ($\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$) that eventually forms over the particle surfaces in the ψ and β phases. Conversely, in the solution with pH 3 at 60 °C, the ψ phase presents the highest R_p values (major corrosion resistance) with respect to the other test conditions, as shown in Figs. 7 and 8.

The corrosion resistance of the ψ phase at pH value of 3 and 60 °C can be explained in terms of the quasicrystalline microstructural instability, specifically that related to defects such as phason [10, 18]. These defects eventually

Table 1 pH values of the solution before and after corrosion testing of β and ψ phases

Phase	Before testing	After testing
ψ	7	8
	3	8
	11	9
β	7	8
	3	6
	11	9

contribute to phase transformations and are sensible increases in temperature. Microstructural changes and the variation in the modulus of impedance values in this type of material are key factors that promote changes in the charge concentration at the double layer and in the charge-transfer corrosion mechanism. However, the increase in temperature also contributes to the formation of highly protective oxides depending on the pH value.

In this investigation, the bayerite in the ψ phase dissolves quickly in the solution at pH value of 3 and 60 °C. The bayerite dissolution leads to the formation of protective oxides. This idea is supported by the literature. For example, Xu *et al.* [19] reported that Al–Cu–Fe nanostructures have coherent metastable precipitates known as Guinier–Preston (G.P.) zones. The precipitates are sensitive to increases in temperature in the range of 22–160 °C. Al-rich phases are preferentially formed, favoring the formation of hydroxides as bayerite.

Conversely, the E_{corr} values obtained for the ψ and β nanostructured phases do not correspond to any bulk pure Al or Al-alloy quasicrystals. These results suggest that the $\text{Al}_{64}\text{Cu}_{24}\text{Fe}_{12}$ and $\text{Al}_{62.5}\text{Cu}_{25.2}\text{Fe}_{12.3}$ nanostructured powders are responsible for the new corrosion potentials reported in this work. This effect is attributed to the large number of superficial atoms developed by the nanostructures formed via mechanical alloying in comparison with conventional macro- and micro (standard sized)-Al alloys.

Fig. 5 Polarization curves for β and ψ phases at room temperature **a** and at 60 °C **b** for different pH values

Fig. 6 R_p of β **a** and ψ **b** phases at room temperature and different pH values

Fig. 7 $|Z|$ versus time for β **a** and ψ **b** phases at 60 °C and different pH values

Fig. 8 R_p versus time of β **a** and ψ **b** phases at 60 °C and different pH values

Tcherdyntsev *et al.* [4] found that the interatomic bonds of quasicrystalline materials are highly saturated, even in surface layers. Consequently, the quasicrystal surfaces are expected to be chemically inert, giving these materials high corrosion resistance. The present results are in agreement with those reported in Ref. [4]. However, the electrochemical test results of this study suggest that the large number of superficial atoms developed by the nanocrystals increase the time required to reach electrochemical equilibrium between anodic and cathodic partial reactions, leading to more positive corrosion potentials values.

Further corrosion studies with different sizes of $\text{Al}_{64}\text{Cu}_{24}\text{Fe}_{12}$ and $\text{Al}_{62.5}\text{Cu}_{25.2}\text{Fe}_{12.3}$ microparticles and nanoparticles will be conducted to corroborate these results.

Furthermore, at 60 °C the $|Z|$ values of the two phases increase by four orders of magnitude, ranging from 87 to 84,000 Ω (Fig. 7). For both phases at pH value of 11 and the ψ phase at pH value of 7, the $|Z|$ values were lower, and there was less variation in the values. The polarization curves (Fig. 5b) and Nyquist diagram (Fig. 9) indicate that the principal corrosion mechanism is charge transfer as indicated by the passivation behavior observed in the

Fig. 9 Nyquist diagrams for β and ψ nanostructured phases at 60 °C and different pH values

polarization curves (Fig. 5b). The R_p results show that the R_p values are higher by three orders of magnitude than those obtained at room temperature (Fig. 8).

Furthermore, the R_p and $|Z|$ values of both phases are well correlated with time at room temperature and the corrosion resistance increase at 60 °C (Figs. 3, 6, 7, 8). These results indicate that the role of temperature in increasing the corrosion resistance is related to the evolution and persistence of particle surface oxides, which are independent of the pH value of solution.

Thermodynamic studies of Fe in Al–Cu–Fe quasicrystalline alloys in contact with water suggest that when temperature increases, the Fe reacts to form iron hydroxides [20]. The hydroxides form a more resistant passive film, diminishing the corrosion process. This result is consistent with the results of the present investigation in which bayerite was formed and dissolved in Al–Cu–Fe quasicrystalline alloys.

Comparing our results with those of Pinheiro and Nascimiento [17, 20] corroborates that the methodology and cell arrangement for the electrochemical techniques employed by the authors in the corrosion study for this type of material was applied correctly.

4 Conclusions

The results of this investigation show that the corrosion resistances of ψ and β nanostructured phases increase with increasing temperature, independent of solution pH. However, the ψ phase exhibits electrochemical stability at 60 °C as illustrated by the changes in $|Z|$ with exposure time. Specifically, the corrosion resistance of the ψ -phase in the solution with pH value of 3 at 60 °C increases more than for any other test condition. This phase also presents special corrosion resistance at acidic condition, retaining all the characteristics of quasicrystalline materials. However, to

confirm this result, microstructural and mechanical tests should be conducted after the corrosion tests.

The predominant corrosion mechanism during the very first hours of solution exposure was controlled by diffusion. After 30 h of exposure to the test solution, the corrosion mechanism changes to charge transfer. The bayerite ($\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$) and iron hydroxides are the principal corrosion products that form at the surfaces of both phases. However, bayerite has poor protective properties regardless of pH value. In contrast, iron hydroxide became more protective with increasing temperature and exposure time for both phases in alkaline and acidic aqueous solutions.

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