Original Article

Precipitation hardening in dilute Al–Zr alloys

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ABSTRACT

The aim of this study was to investigate the effect of solute content (hipoperitectic Al–0.22 wt.%Zr and hyperperitectic Al–0.32 wt.%Zr) on the precipitation hardening and microstructural evolution of dilute Al–Zr alloys isothermally aged. The materials were conventionally cast in a muffle furnace, solidified in a water-cooled Cu mold and subsequently heat-treated at the temperature of 650 K (377 °C) for 4, 12, 24, 100 and 400 h. Mechanical characterization was performed at room temperature, using a microhardness tester and microstructural characterization was carried out on a Transmission Electron Microscope – TEM. The observed microhardness values increased during isothermal aging, due to the precipitation of nanometer-scale Al2Zr L12 particles. Peak strength was achieved within 100 h of aging. After aging for 400 h, microhardness values presented a slight decrease for both alloys, thus indicating overaging due to the coalescence of precipitates. Microhardness values increased with solute content, due to the precipitation of a higher number density of finer precipitates. After 400 h of heat-treating, coalescence was higher for the alloy with lower solute content and, also, the presence of antiphase boundaries – APBs, planar faults associated with the L12 to D03 structural transition, were observed. Comparing theoretical calculations of the increment in strength due to precipitation strengthening with experimental results, it was observed that their values are in reasonable agreement. The Orowan dislocation looping mechanism takes place during precipitation hardening for both alloys in the peak hardening condition.

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1. Introduction

Al alloys with additions of elements of group IV of the periodic table (Ti, Zr and Hf), present potential as structural materials at high temperatures, because they present low solid diffusivity, form compounds of high symmetry, present low density, high melting point and low precipitate/matrix mismatch [1–4].

Among these elements, the addition of Zr in Al present low solid solubility, lower solute segregation [3,4] and precipitate the metastable Al2Zr with L12 structure (fcc) [5–7]. Such particles provide hardening to the material for periods longer than 400 h [4], what is not achieved by other additions, such as Ti, Sc, Er or Hf [8–10].

The Al3Zr L12 present low coarsening kinetics [11] and maintains metastability to reported aging times of 1600 h [12], at temperatures up to ~0.75Tm [4]. The Al3Zr equilibrium structure is tetragonal DO23 [13] and was only observed at aging temperatures lower than ~773 K in cold-worked alloys [11].

There are studies indicating the use of Al–Zr based alloys as heat-resistant electrical conductors [14], and in the aerospace and automotive industries, at temperatures up to 673 K [15]. If these Al alloys can replace more expensive materials such as Ti alloys, used in aircraft and Al Alloys Steel Reinforced conductors (ACSR), used in overhead transmission lines, this may represent great cost reduction.

Due to solute distribution during solidification, Al–Zr alloys present segregation along dendrites. The Zr content in the center of the dendrites can be two-fold the nominal alloy composition [16], and in this case, over the maximum solid solubility of 0.28 wt.%Zr [17]. For this reason, it is common practice not to perform solution heat-treatments in such alloys in order to preserve its mechanical properties, as can be seen elsewhere [4,6,7,15].

During aging, as precipitates nucleate, the material experience an increase in strength, that depends on the precipitation strengthening mechanisms acting in the alloy. These depend on properties such as particle size, volume fraction, and structure, as can be seen elsewhere [5,8]. Therefore, knowing these properties and the theoretical contributions to the increase in strength in an alloy is an important factor to understand the potential for precipitation hardening.

The aim of this study was to analyze the effect of solute content on the age hardening and microstructural evolution of dilute Al–Zr alloys (conventionally cast Al–0.22 wt.%Zr and Al–0.32 wt.%Zr alloys artificially aged at 650 K), by analyzing its microhardness, microstructural evolution during aging and comparing theoretical values of the increment in strength due to precipitation hardening mechanisms with experimental results.

2. Experimental

For the preparation of the alloys, high purity Al (Al > 99.8 wt.%) and an Al–10 wt.%Zr master alloy waffle, were used. The materials were cast in a muffle furnace at the temperature of 1120 K, followed by stirring, degassing with inert gas (Ar) and pouring into a water-cooled Cu mold. Chemical analysis of the Al–0.22 wt.%Zr alloy was performed in an optical mass spectrometer and in an inductively coupled plasma optical emission spectrometer, for the Al–0.32 wt.%Zr alloy (Table 1).

The cast ingots had a mass of ~600 g, and were sectioned to 10 mm cubic samples that were randomly selected for heat-treating in a muffle furnace, at the temperature of 650 K (±1 K) for 4, 12, 24, 100 and 400 h. After treatment, samples were quenched in water at room temperature.

Microhardness tests were performed on metallographically polished samples, with a 1.96 N load and 5 s of dwelling time. 20 microhardness tests were performed on each sample, providing average and standard deviation values.

The microstructural analysis was carried out using a JEOL JEM 1011 Transmission Electron Microscope – TEM, with 100 kV of accelerating voltage. TEM samples were first ground to thin discs with thickness of 100 μm, subsequently being electropolished in a Struers Tenupol 5 twin-jet machine, operating at the temperature of 276 K (±3 K); (3 °C ± 3 °C), with an operating voltage of 8 V. The electrolyte used is constituted of nitric acid (1/3) and methyl alcohol (2/3). After electropolishing, the samples were rinsed three times in methanol and methyl alcohol cups, in a procedure similar to the one used by Ünlü [18]. The radii of the precipitates were measured using ImageJ software and statistical analysis was carried out in R statistical.

3. Results and discussion

3.1. Age hardening

Fig. 1 displays the evolution of microhardness of the studied alloys. The precipitation kinetics for both alloys is similar, with both materials achieving peak hardness at 100 h and overaging occurs at 400 h. Hardening occurs due to the precipitation of Al3Zr. The difference between the two alloys in Fig. 1 is the magnitude of the hardness values, once the

| Table 1 – Chemical composition of the studied alloys (in wt.%). |
|----|----|----|----|----|
| Alloy | Zr | Fe | Si | Al |
| Al–0.22Zr | 0.23 | 0.10 | 0.05 | Balance |
| Al–0.32Zr | 0.32 | 0.10 | 0.03 | Balance |

Fig. 1 – Variation of Vickers microhardness (HV0.2) of the studied alloys as a function of aging time at 650 K.
Al-0.32 wt.%Zr alloy present greater solute content, its chemical driving force for precipitation is higher, leading to a higher density of smaller precipitates [4], which can provide greater microhardness.

The precipitation kinetics of the studied materials is remarkably slow compared to conventional Al alloys. The latter alloys start to overage at lower temperatures and at shorter heat-treating periods [19-21]. In Fig. 1, at the second y axis, microhardness values were converted to MPa, using a chart [16].

Fig. 2 presents TEM dark-field micrographs of the Al-0.22 wt.%Zr alloy (a) aged for 100 h and (b) aged for 400 h. In Fig. 2a it is evident spherical nano-scale Al3Zr precipitates homogeneously distributed in the Al matrix. Measurements show that the mean precipitate radius \( \langle r \rangle \) is \( 6.7 \pm 1.0 \) nm. In Fig. 2b there are two groups of spherical precipitates. The smaller ones present: \( \langle r \rangle = 6.5 \pm 1.8 \) nm and the bigger particles: \( \langle r \rangle = 1077 \pm 20.7 \) nm. The former particles present an \( \langle r \rangle \) equal to the ones of samples aged for 100 h, although they have a higher standard deviation. The latter precipitates had probably nucleated into regions of lower solute content, what led to a lower number density of particles with bigger \( \langle r \rangle \) [4], which had further increased during aging. Such are possibly growing at the expense of the smaller precipitates, as described by the Gibbs-Thomson effect [22].

The larger precipitates in Fig. 2b present a line of no contrast, as indicated by arrows. This is an APB, a planar fault that can occur in ordered precipitates, and is associated with the beginning of the \( \text{L1}_2 \rightarrow \text{DO}_{23} \) transition [23]. In such structural change, the Al3Zr precipitate changes its structure from metastable face centered cubic to stable tetragonal, but its stoichiometry remains unchanged [16]. Such structural transition happens when an APB is formed with a dislocation vector of \( \vec{b} = a/2 \langle 110 \rangle \) in \( \{100\} \) planes [11,24,25]. Although the beginning of the transition was observed, the Selected Area Diffraction Pattern – SADP of Fig. 2b shows that the diffraction pattern is still consistent with the \( \langle 112 \rangle \) zone axis of the Al3Zr \( \text{L1}_2 \), as found by other authors for similar aging conditions [11,13,23,26].

Fig. 3 presents TEM images of the Al-0.32 wt.%Zr alloy. Fig. 3a is a bright-field micrograph of a sample aged for 100 h, and Fig. 3b is a dark-field image for a sample aged for 400 h. Fig. 3a shows homogeneously distributed precipitates, that present an average mean radius: \( \langle r \rangle = 3.1 \pm 0.4 \) nm. Such
precipitates are smaller than in the Al–0.22 wt.%Zr alloy in the same aging condition, therefore explaining the higher micro-hardness values.

In Fig. 3b, precipitates present \( r = 7.5 \pm 2.4 \text{ nm} \). No APBs were observed in this condition. The SADP of Fig. 3b indicates a [001] zone axis of Al\(_2\)Zr L1\(_2\).

Fig. 4 presents TEM micrographs of an Al–0.32 wt.%Zr alloy. Fig. 4a is a bright-field image of sample aged for 400 h and Fig. 4b is its complementary dark-field. Fig. 4a was taken on an interdendritic region and, like in Fig. 2b, shows a lower density of bigger, spherical precipitates, (comparing with Fig. 3b). Such region presents a lower volume fraction of solute, what also favors the precipitation of rod-like Al\(_2\)Zr precipitates (indicated by arrows) [12].

3.2. Precipitation hardening mechanisms

In precipitation hardening, there are interactions between dislocations and precipitates. Such interactions depend on particle size, spacing, alloy composition, crystallographic orientation between precipitate and matrix and aging parameters [27,28]. Precipitates are barriers that can be bypassed or sheared by dislocations. In the first case, the dislocation bends itself due to the applied tension during the contact with the precipitate, resulting in the bypassing of the precipitate and letting a dislocation loop around it. In the second case, the shearing of the particle occurs as the dislocation moves through the crystal, what can happen only when the precipitate is coherent with the matrix [28].

Eq. (1) presents the increment in strength of a material due to the Orowan dislocation looping mechanism (\( \Delta \sigma_{ow} \)), where \( M = 3.06 \) is the Taylor factor of the matrix [29], \( G_{Al} = 25.4 \text{ GPa} \), the shear modulus of the matrix [30], \( b = 0.286 \text{ nm} \) the Burgers vector [31], \( \nu_{Al} = 0.345 \) is the Poisson ratio of the matrix [32] and \( \langle r \rangle \) the mean precipitate radius [27]. \( L \) is the effective inter-precipitate spacing (Eq. (2)), where \( f \) is the precipitate volume fraction [33]. Adopting \( \langle r \rangle \) values from 1 to 100 nm, based on literature values [11,25,26,34], and \( f \), usually a value between 0.2 and 1.0% for Al–Zr alloys [5,11,12,35], it is possible to calculate the theoretical contribution of \( \Delta \sigma_{ow} \) to strengthening, as a function of \( \langle r \rangle \), adopting the equilibrium value of \( f = 0.2\% \) (from the lever rule), as shown in Fig. 5.

\[
\Delta \sigma_{ow} = M \left( \frac{0.8G_{Al}b}{2\pi(1-\nu_{Al})^{1/2}} \right) \ln \left( \frac{2\langle r \rangle}{b} \right) \quad (1)
\]

\[
L = \left( \sqrt{\frac{2\pi f}{3f}} - \frac{\pi}{2} \right) \langle r \rangle \quad (2)
\]

Among the shearing mechanisms, three will be considered: (i) modulus hardening, (ii) coherency strengthening and (iii) order strengthening.

(i) Modulus hardening occurs when a dislocation reaches the external surface of a precipitate and starts shearing it. The contribution of this mechanism for the increase in strength of the material – \( \Delta \sigma_{mod} \) (Eq. (3)) [33] is proportional to the difference between precipitate and matrix shear moduli (Eq. (4)) [33], where \( G_{p} = 68 \text{ GPa} \) [30] and \( \Gamma \) is the dislocation line tension (Eq. (5)) [27]. Substituting the constants in the equations
and using the values of \(r\) and \(f\) used in Eq. (2), the theoretical values for \(\Delta \sigma_{\text{mod}}\) are shown in Fig. 5.

\[
\Delta \sigma_{\text{mod}} = 5.5 \times 10^{-3} M_b (\Delta \sigma)^{3/2} \left( \frac{f}{\nu} \right)^{1/2} \left( \frac{r}{b} \right)^{0.275}
\]  
(3)

\[
\Delta G = \left[ G_p - G_{\text{Al}} \right]
\]
(4)

\[
\tau' \approx \frac{G_{\text{Al}} b^2}{2}
\]  
(5)

(ii) Coherency strengthening is originated by the interactions between precipitate stress fields with dislocations. In coherent precipitates, the lattice is continuous along the precipitate/matrix interface, but as the particle loses coherency, it gives rise to interfacial dislocations [36], those can interact with a moving dislocation, repelling it. The increase in strength due to this mechanism (\(\Delta \sigma_{\text{coh}}\)) is given by Eq. (6), where \(\chi = 2.6\) is a constant \([33]\) and \(\epsilon\) (Eq. (7)) \([27, 33]\) is a misfit parameter, where \(\nu_b = 0.240\) \([37]\) is the precipitate Poisson ratio, that is dependent of the absolute precipitate/matrix misfit (\(\delta\) (Eq. (8))) \([26]\), where \(a_{\text{Al}} = 4.0495\ \text{Å}\) \([38]\) and \(a_p = 4.08\ \text{Å}\) \([26]\) are Al and Al1Zr L12 lattice parameters, respectively. The contribution of \(\Delta \sigma_{\text{coh}}\) for strengthening is presented in Fig. 5.

\[
\Delta \sigma_{\text{coh}} = M_b \left[ \epsilon (a_{\text{Al}} - a_p) \right]^{1/2} (\nu_b G_{\text{Al}} / \tau')^{1/2}
\]
(6)

\[
\epsilon = \left| \frac{1}{1 + 2 G_{\text{Al}} (1 - 2 \nu_p) / G_{\text{Al}} (1 + \nu_p)} \right|
\]
(7)

\[
\delta = \frac{a_{\text{Al}} - a_p}{a_{\text{Al}} + a_p}
\]
(8)

(iii) In Order strengthening, APBs have an important role. In ordered alloys they can be formed during an order-disorder transformation or by shearing [39]. Among the most important Engineering alloys hardened by this mechanism, there are Ni super alloys and stainless steels, because they present precipitates with the L12 ordered structure. The hardening by this mechanism occurs when a dislocation shears an ordered precipitate, creating an APB in its glide plane [33]. In this case, APBs are created as a result of successive shearing of dislocations with a Burgers vector of \(1/2 \langle 110 \rangle\) gliding on different \((111)\) planes [5]. The energy per area unit in this plane; \(\gamma_{\text{APB}} = 0.445\ \text{J/m}^2\) is the energy by area unit opposing dislocation motion when the defect penetrates the precipitate [5]. The increase in strength due to chemical order (\(\Delta \sigma_{\text{ord}}\)), is given by Eq. (9) \([33]\) and its contribution to strengthening is shown in Fig. 5, for \(f=0.2\%\).

\[
\Delta \sigma_{\text{ord}} = M \frac{\gamma_{\text{APB}}}{2 b} \left( \frac{3 \sqrt{3} f}{2 \nu_{\text{Al}} b} \right)^{1/2}
\]
(9)

It is possible to compare the theoretical strengthening mechanisms with experimental values, as shown in Fig. 5, using Eqs. (1), (3), (6) and (9), the experimental results of \(\tau\) for the peak aged alloys (aging for 100h) – white and black circles in Fig. 5, and its respective Vickers microhardness values, using a conversion factor of 1/3 from microhardness to strength [40], a literature experimental value – diamond with crossed lines [35] and the equilibrium volume fraction of precipitates for 650K, calculated by the lever rule: \(f=0.002\).

Several authors studied the precipitation strengthening mechanisms in Al–Zr based alloys \([5, 8, 35, 41–43]\). In Fig. 5, for any given \(\tau\), the predominant strengthening mechanism will be the one who provides the lowest contribution to \(\Delta \sigma\) [5,35].

In Fig. 5, hardening should be caused first by the component \(\Delta \sigma_{\text{mod}} + \Delta \sigma_{\text{coh}}\), until \(\tau \sim 1.4\ \text{nm}\), when the \(\Delta \sigma_{\text{mod}} + \Delta \sigma_{\text{coh}}\) line intersects with \(\Delta \sigma_{\text{ord}}\), the latter mechanism should be responsible by hardening until \(\tau \sim 3.1\ \text{nm}\. After this threshold value, it is no longer possible for a dislocation to shear a precipitate, so \(\Delta \sigma_{\text{pw}}\) will be activated. The experimental values plotted in Fig. 5 show that \(\Delta \sigma_{\text{pw}}\) is the active mechanism for the studied alloys. The theoretical limit of 3.1 nm precipitate radius for shearing in Fig. 5 is near the experimental limit of 2.8 nm, observed with HAADF-STEM (High Angle Annular Dark-Field Scanning Transmission Electron Microscopy) techniques [5].

Other studies [5,41] about the precipitation of Al13Zr L12 and Al12Sc(Zr) L12, respectively, used a model distinct of the used in this work to study order strengthening and they suggest that it is possible that such mechanism can be responsible for hardening during all the shearing process. Also, there are claims that the active strengthening mechanism during shearing of Al12Sc(Zr) L12 and Al12Sc L12 precipitates, will be the one with greater contribution between \(\Delta \sigma_{\text{mod}} + \Delta \sigma_{\text{coh}}\) and \(\Delta \sigma_{\text{ord}}\) [8,42,43].

In Fig. 5, it is observed that \(\Delta \sigma_{\text{pw}}\) is the predominant mechanism for the studied alloys. The differences between the theoretical and experimental values of \(\Delta \sigma\) can be explained in terms of solute segregation during solidification. Once the alloys were not solution treated, its solidification segregation profile remained throughout the microstructure, what leads to a higher number density of intradendritic precipitates (Fig. 3), compared to the interdendritic zones (Fig. 4) [16]. Hence the lack of precipitates along the grain boundaries might be a deleterious factor for strength [16].

It is possible to observe in Fig. 5 that there is a theoretical range of \(1.4<\tau<3.1\ \text{nm}\, \text{where} \, \Delta \sigma\text{ is optimum. Processing routes for Al–Zr alloys that produce particles out of this range will lead to materials with lower} \Delta \sigma\text{.}

Also in Fig. 5, the experimental value from the Al–0.32Zr–0.17Sc (in wt.%), alloy aged at 573K for 3h [35], presented a greater increase in strength than the alloys from this study. Besides, the use of a lower aging time (3h), the alloy presented \(f=0.003\) of Al13Sc(Zr) L12 precipitates with \(\tau = 1.5\ \text{nm}\). The reasons for the greater value of \(\Delta \sigma\) can be explained in terms of chemical driving force, which increases with lower aging temperatures, and higher solute content [4]. It is possible to observe in Fig. 5 that the operating strengthening mechanism in the Al–0.32Zr–0.17Sc alloy is \(\Delta \sigma_{\text{ord}}\), due to its lower \(\tau\).

Depending on the alloy composition and aging parameters, the strengthening mechanisms might be distinct from the ones presented in this study, e.g., a component due to stacking fault strengthening may be present in alloys in which precipitates undergo structural transitions [1,33].
4. **Conclusion**

- Microhardness values increased with solute content, due to the precipitation of finer Al$_2$Zr L1$_2$ precipitates. Such microhardness values increased with aging time, until reaching peak hardness at 100 h, thus exhibiting a slow precipitation kinetics;
- The alloys experienced a slight decrease in microhardness only after 400 h of aging, therefore, indicating that even dilute Al–Zr alloys present elevated thermal stability;
- The microstructure of the studied alloys presented homogeneously distributed Al$_2$Zr ordered precipitates. At the intradendritic regions, a higher number density of spherical particles is present. At the interdendritic regions, there is a lower density of bigger spherical and rod-like precipitates;
- After 400 h of aging, the precipitates in the Al–0.22 wt.%Zr alloy presented antiphase boundaries, a structure associated with the beginning of the L1$_2$ $\rightarrow$ D0$_{22}$ transition, although the latter structure was not found;
- The theoretical contributions to the increase in strength due to precipitation hardening in Al–Zr alloys indicate that there is a range of 1.4 < \( r \) < 3.1 nm where the increment in strength is higher and constant, due to Order strengthening.

**Conflicts of interest**

The authors declare no conflicts of interest.

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