J Mater Sci (2012) 47:6206–6212
DOI 10.1007/s10853-012-6494-z

Superplastic behavior of Zn–Al eutectoid alloy with 2 % Cu

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Received: 12 March 2012 / Accepted: 10 April 2012 / Published online: 30 May 2012

Abstract The effects of deformation temperature and strain rate on the superplastic behavior of the Zn–21Al–2Cu alloy (Zinalco alloy) were investigated by uniaxial tensile tests. Results were compared with those of the Zn–22Al eutectoid alloy without Cu. It was observed that additions of 2 % Cu leads to a decrease of the maximum strain attainable from 2600 % to 1000 %. The maximum strain in Zinalco alloy is obtained at lower strain rates. The presence of Cu increases the values of flow stress up to 600 % compared with those reported in the Zn-22Al alloy. Grain size sensitivity (p), true activation energy (Q_t), and constant A of the constitutive equation were not affected by presence of Cu unlike the stress exponent (n) which increased from 2.5 to 3.9. The main effect of Cu was to decrease the plastic flow stability of the Zn–22Al alloy. The results indicate that presence of Cu in the Zinalco alloy causes a hardening effect at low strain rates leading to a decrease in the strain rate sensitivity which promotes the formation and growth of sharp necks. Microstructural characterization suggests that the large deformations at necking could possibly be due to the substantial elongation capability of the Zn-rich phase (η).

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Introduction

A superplastic material is capable of being formed to high strains without the formation of unstable tensile necks. When an alloy exhibits superplastic behavior, there is a possibility of using this material to fabricate complex components in a simple forming process [1, 2]. Classical example of a superplastic material is the Zn–Al eutectoid alloy (Zn–22Al) [1, 2]. The maximum strain attainable during tensile deformation of this alloy depends critically on the strain rate, testing temperature, and the initial grain size [1–10]. Strains up to 3,000 % have been observed in a region where the relationship between flow stress and strain rate exhibits a maximum slope (region II) [1–10]. In this region, deformation is essentially uniform up to at least 800 % [11]. However, because of their low mechanical strength at room temperature, the applications of superplastic Zn–22Al alloys have been limited to fabricate components used in office equipment and instrument covers [12].

Alloying elements such as Cu and Ag have been used to enhance the mechanical properties of this alloy [13, 14]. By adding 2 % Cu, the Zn–21Al–2Cu alloy (Zinalco alloy) can be obtained. This alloy has a unique combination of properties midway between those of aluminum and ductile iron [15]. Its high strength, good machinability, and toughness allow the alloy to be used for the fabrication of products such as tubes handrails and architectural profiles which are obtained through several processes including smelting, injection, extrusion, and rolling operations [15, 16].

Zinalco alloy exhibits superplastic behavior during tensile testing at room temperature [17]. It shows a maximum attainable strain close to 200 % [17]. The effect of Cu on the superplastic behavior of Zn–22Al alloys has only been reported for amounts of Cu ranging from 0.13 % to 0.5 % [18, 19]. However, for these low contents, there has not been observed a significant effect of this alloying element on the superplastic characteristics of the alloy [18, 19].

The aim of this investigation is to evaluate the superplastic behavior of Zn-21Al-2Cu alloy (Zinalco alloy) at high temperature. The results obtained are compared with those of the Zn–22Al alloy to study the effect of Cu on the superplastic properties of this alloy.

Experimental procedure

The Zn–21Al–2Cu alloy (Zinalco alloy) was prepared by melting Zn, Al, and Cu of high purity in an induction furnace. A 38-mm diameter cylindrical rod was obtained by continuous casting. The rod was cut, extruded at 563 K, and rolled at 513 K to obtain rolled sheets of 2.54-mm thickness. Specimens for tensile testing with a gage length (L_0) of 6.35 mm were machined from the rolled sheets. After machining, specimens were solution treated at 623 K during 1 h. Then, they were quenched in ice water at 288 K. A fine-grained microstructure with an average grain size of 1 µm was obtained in all specimens. Grain size measurements were performed by the intercept method.

To evaluate the grain size sensitivity parameter (p), some quenched specimens were additionally annealed at 523 K for 5 hr and 91 hr to produce equiaxed microstructures with average grain size of 3.35 and 4.5 µm respectively. After heat treatments, specimens were polished and then tested in tension. Experiments were performed at constant crosshead speed in a universal testing machine equipped with a thermostatic chamber. Specimens were deformed to fracture. Tensile test were carried out utilizing three temperatures in the range from 413 K to 513 K and initial strain rates, calculated from the initial gage length of specimen, in the range from 10^{-3} s^{-1} to 1 s^{-1}. This range corresponds to the region II reported in other work for the Zn–22Al alloy with a grain size of about 1 µm [5]. Before tensile deformation, specimens were heated at 30 °C/min and held during 20 min at the established testing temperature. Microstructure of specimens before and after deformation was characterized by scanning electron microscopy (SEM) and X-ray diffraction (XRD).

Results

Initial microstructure

Figure 1a shows the microstructure of specimens after solution treatment and quenching. It is observed a very fine and homogeneous mixture of α and η, which are Al- and Zn-rich phases (dark and bright phases, respectively). These phases result from a transformation that occurs in the Zn–Al system: β (triclinic) → η (hcp) phase + R (rhombohedral). In this phase transformation, R represents a transition phase which transforms to η (hcp) + α (fcc) [20]. The presence of these phases (α, η) is confirmed by XRD showed in Fig. 1b, which also show a peak correspond at τ' intermetallic phase (Al_2Cu_3Zn). The amount of τ' phase is so small that cannot be identified in SEM.

A fine-grained microstructure as the one observed in Fig. 1a is needed to obtain superplastic deformation. It is well known that a fine grain size (<10 µm) helps to increase the fraction of boundaries, which lead to a situation where deformation is carried out with more facility through to these boundaries [21].

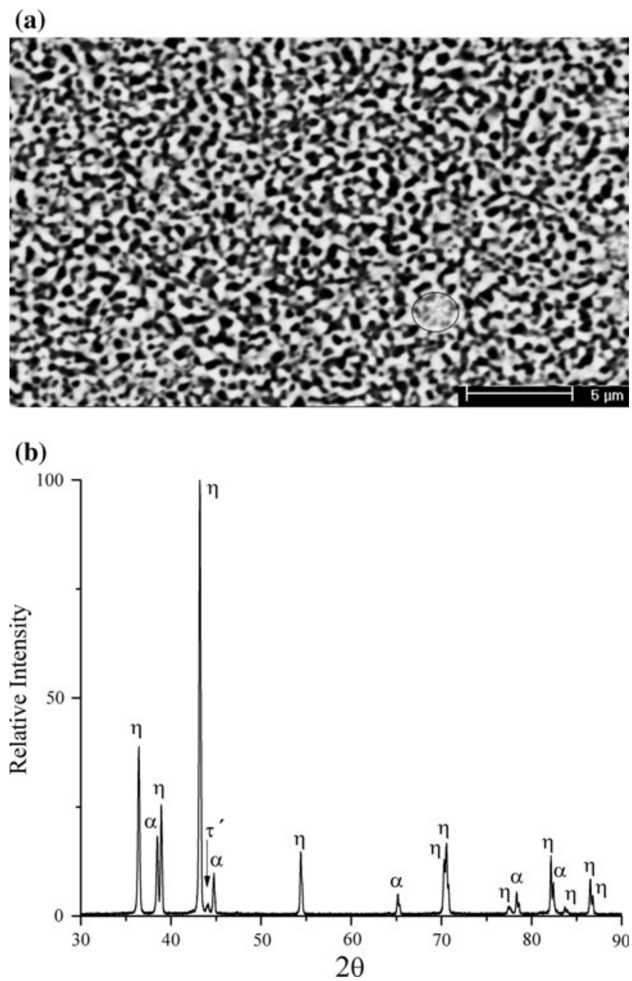

Fig. 1 **a** SEM micrograph of Zn–21Al–2Cu alloy (Zinalco alloy) after solution treatment and subsequent quenching showing a mixture of fine α and η. **b** XRD pattern which confirms presence of α, η

Superplastic behavior

Figure 2a shows the effect of the strain rate on the total strain attainable of specimens (with grain size of 1 μm) tested at 413, 463, and 513 K. As can be seen, Zinalco alloy exhibits superplastic behavior in the range of the strain rates investigated. For three temperatures, total strain exhibits a maximum with the lowest strain rate used (10^{-3} s^{-1}). However, with increments in the strain rate, the total strain achieved decreases. It can be seen in this figure that the maximum strain attainable was about 1,000 % at 513 K and 10^{-3} s^{-1}. However, this strain is lower than that reported for commercial and high-purity Zn–22Al alloy (2,600 %) [9], and that observed in alloys with concentrations of Cu up to 0.5 % (1,950 %) [18].

Figure 2b shows the variation of the flow stress as a function of strain rate. It is observed a linear relationship between the flow stress and the initial strain rate. This observation is in agreement with the region II reported for the Zn–22Al alloy [5] and the Zn–22Al alloy doped with Cu [19, 20]. The strain rate sensitivity (m), measured from the slope of lines presented in Fig. 2b, was about 0.26. This value is lower than that reported for the Zn–22Al alloy ($m = 0.4$–0.5) [1, 2, 5–10].

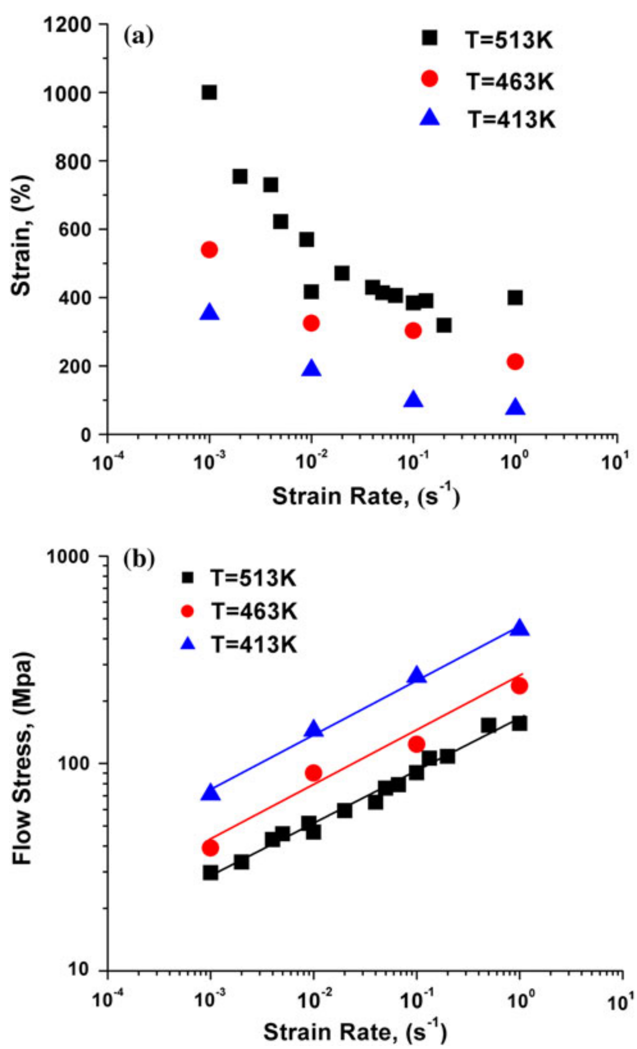

Fig. 2 **a** Total strain and **b** flow stress as function of the strain rate and testing temperature of Zn–21Al–2Cu alloy (Zinalco alloy)

Figure 3 illustrates the variation in final length of specimens as a function of temperature and strain rate, Fig. 3a, b, respectively. Letter A shows undeformed specimen and letters B–E show specimens deformed to fracture at different strain rates. As can be seen, there is a considerable effect of the variables investigated on the final length of specimens. When deformation is carried out at the lowest temperature (413 K) and the highest strain rate (10^{-1} s^{-1}), lowest elongation is observed (Fig. 3a, letter B). For the same temperature but with lower strain rates, specimens exhibit higher elongation to failure and a ductile fracture is observed (Fig. 3a, letters C–E).

Specimens deformed at 513 K exhibit a ductile fracture for all of the strain rates investigated. For a given strain rate, the elongation to fracture at 513 K was higher than those observed at 413 K (compare Fig. 3a, b, letters B–E). The higher degree of sharpness at necking was observed at low strain rates in specimens deformed at 513 K (Fig. 3b, letters C and D). In addition, the fracture of specimens tested at the lowest strain rate (10^{-3} s^{-1}) and the highest temperature (513 K) was characterized by two types of necks along the gage length: a sharp-shaped neck in adjacent gripping areas and a more diffuse neck in the central part (Fig. 3b, letter E).

It was observed during tensile tests that even at early stages of deformation, there are significant deviations from stable and uniform plastic flow. These observations are consistent with the low value of the strain rate sensitivity parameter (m) calculated for this alloy (0.26). The low value of m observed in Zinalco alloys results from an increase of the flow stress, which is higher at low strain rates (i.e. 10^{-3} s^{-1}). At this rate, the flow stress Zinalco alloy increases up to 600 % compared with the reported value of the Zn–22Al alloy [1, 2, 5–10].

Determination of superplastic parameters

In steady state conditions, strain rate can be represented by the following dimensionless equation:

$$\dot{\varepsilon} = ADGb/kT(b/d)^p(\sigma/G)^n \quad (1)$$

where D is the diffusion coefficient [$D = D_0 \exp(-Q/RT)$, D_0 is the frequency factor, Q is the activation energy, R is the gas constant, and T is the absolute temperature], G is the shear modulus, b is the Burgers vector, k is the Boltzmann's constant, d is the grain size, σ is the flow stress, p is the grain size sensitivity, n is the stress exponent, and A is the dimensionless constant [1, 2, 21].

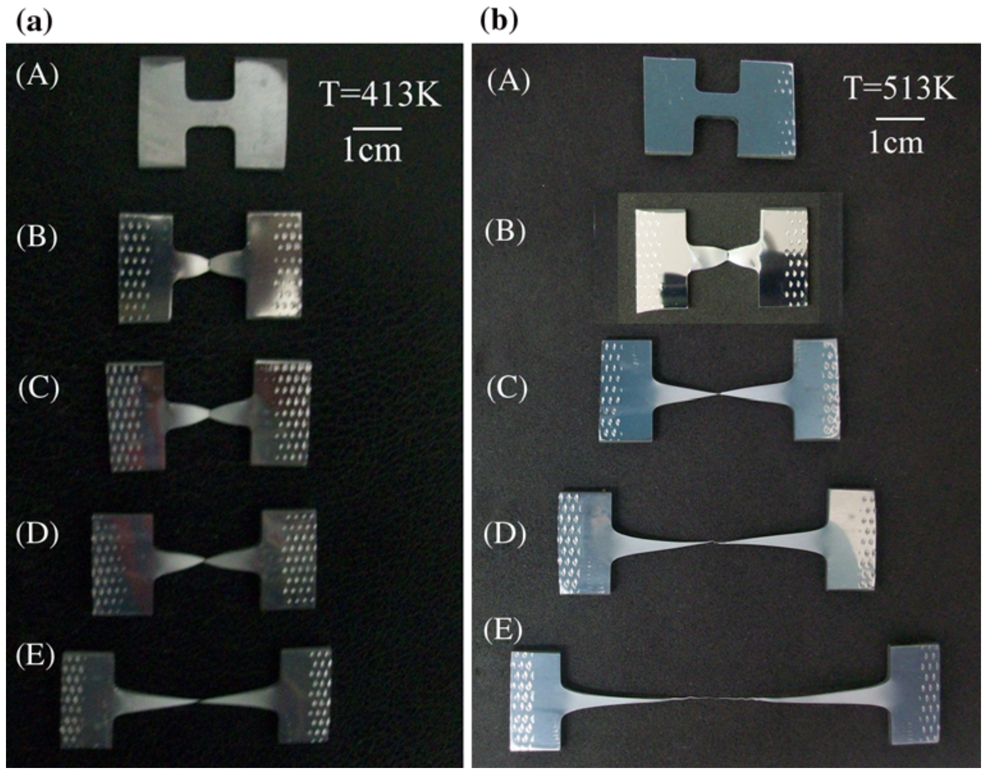

Fig. 3 Tensile specimens of Zn–21Al–2Cu alloy (Zinalco alloy) tested at: **a** 413 K and **b** 513 K. Incises: *A* Without deformation and deformed to fracture at a strain rate of: *B* $10^{0}\ s^{-1}$, *C* $10^{-1}\ s^{-1}$, *D* $10^{-2}\ s^{-1}$, and *E* $10^{-3}\ s^{-1}$

Under any selected experimental conditions, superplastic behavior is characterized by the values of n, p, Q, and the constant A of Eq. 1. It has been established that region II of Zn–22Al alloy is characterized by values of n and p in the range of 2–2.5 [6, 7, 9, 10, 22]; a value of Q close to the needed for grain boundary diffusion [6, 7, 9, 10, 22] and a value of A of approximately 10^6 [22].

In order to evaluate the effect of an addition of 2 % Cu on the superplastic properties of Zn–22Al alloy, these parameters were determined for the alloy used in this work. The stress exponent (n) in tension was obtained as $n = 1/m$, where m represents the slope of a line presented in Fig. 2b. The values of n obtained were found to be in the range from 3.76 to 3.96. To determine the grain size sensitivity parameter (p), additional tensile tests were performed at 513 K in specimens with initial grain sizes of 3.35 and 4.5 µm. The value $p = 2.0$ was obtained from the slope of lines presented in Fig. 4a (log σ^n vs. log d at $10^{-3}\ s^{-1}$).

The true activation energy (Q_t) was determined by plotting σ^n/G^{Tn-1} versus $1/T$ (Fig. 4b). Therefore, temperature dependence of shear modulus was considered. The average value obtained for Q_t was 75.1 ± 2.45 kJ/mol. This value is close to that reported in Zn–22Al alloy (70–81 kJ/mol) [6, 7, 9, 10, 22] and to that of Zn–22Al alloy doped with Cu (88 kJ/mol) [18]. The Q_t values obtained in this investigation can be compared with the one for grain boundary diffusion in pure Zn (60 kJ/mol) and in pure Al (69 kJ/mol).

The data presented in Fig. 2b were normalized according to Eq. 1 by plotting $(\dot{\varepsilon}kT/D_{gb}Gb)\ (d/b)^p$ versus σ/G in a logarithmic scale as shown in Fig. 5. For this plot, D_0, Q_{gb}, b and p were 1 cm^2/s [9], 75.1 kJ/Mol, 2.86×10^{-8} cm and 2.0, respectively. The normalized data for the three different temperatures in Zinalco alloy cluster, about a single-straight line that extends to five orders of magnitude of the strain rate. The slope of this line was 3.88 ± 0.1, which corresponds to the stress exponent (n). These results show that n is not a continuous function of temperature and confirm the increase of n from 2.5 to 3.9.

The experimental constant A was determined using data of Fig. 2b and parameters n, p, and Q. The value of this parameter calculated for the Zinalco alloy was 3.4×10^6. Values of A for the Zn-22Al alloy with Cu additions have not been reported, however the value obtained in this investigation with additions of 2 % Cu (3.4×10^6) is close to the value reported for the Zn-22Al alloy (1.1×10^6) [22]. The changes in the A value occur mainly as consequence of changes in other parameters of Eq. 1.

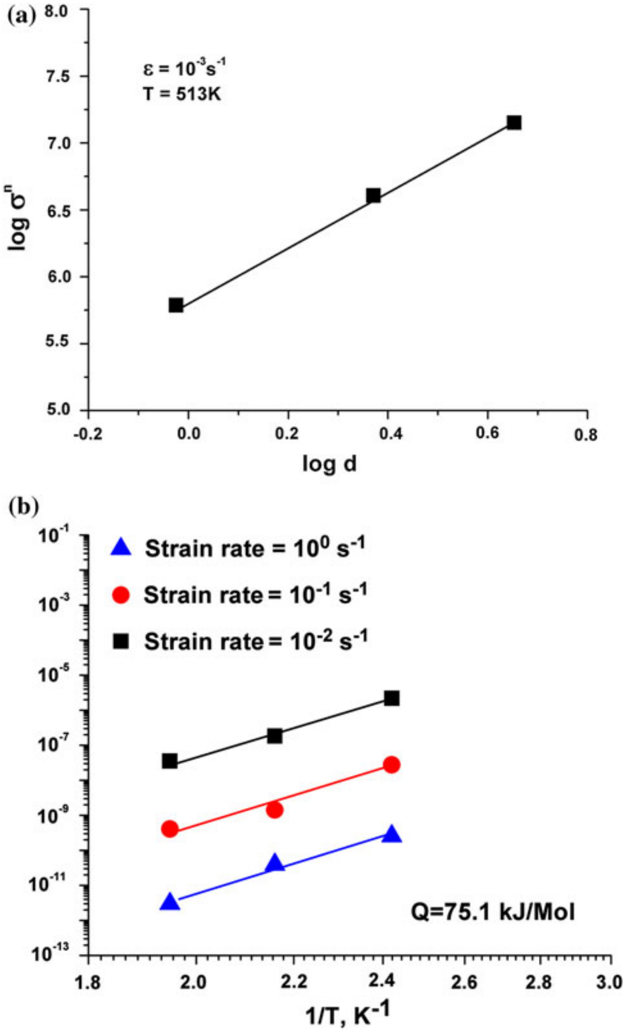

Fig. 4 **a** Determination of grain size sensitivity p and **b** true activation energy Q_t in Zn–21Al–2Cu alloy (Zinalco alloy)

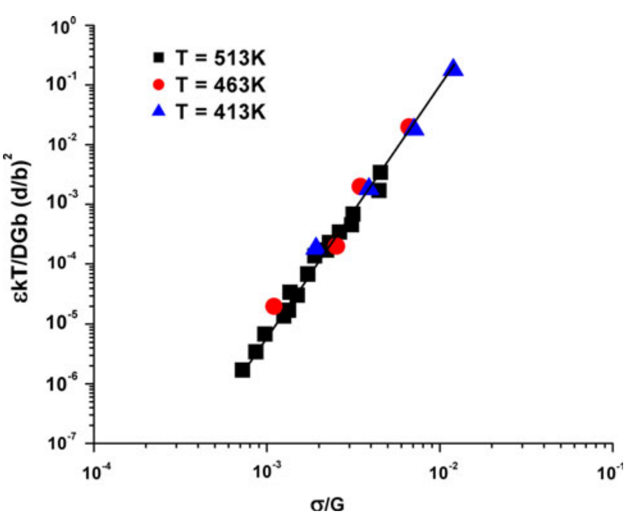

Fig. 5 A plot of normalized strain rate versus normalized flow stress in a logarithmic scale for Zn–21Al–2Cu alloy (Zinalco alloy)

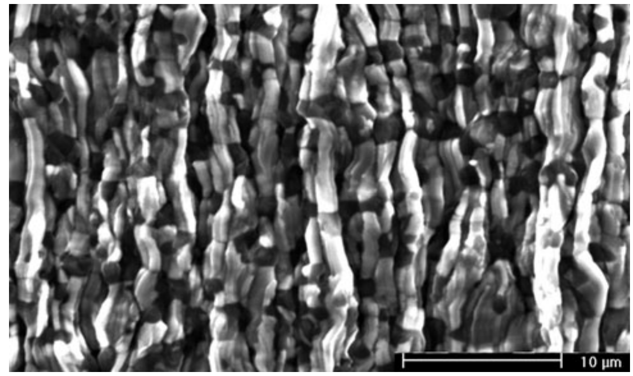

Fig. 6 SEM micrograph of Zn–21Al–2Cu alloy tested at 513 K and 10^{-3} s^{-1} showing grains alignment (*resembling flow bands*) parallel to the tensile direction

Microstructure after deformation

Figure 6 shows microstructure of specimen tested at 513 K and 10^{-3} s^{-1}. A comparison of the microstructural features, observed before and after deformation, suggests that the η phase exhibits a substantial elongation capability compared with the α phase. As can be seen in Fig. 6, the large bright-colored grains that correspond to η-phase are alternated with small-equiaxed grains of α-phase. In general, these two phases exhibit larger grain size than that observed before deformation at 513 K. The mean grain size was measure as 1.25 mm, it is observed that both α and η grains are aligned (resembling flow bands) parallel to the tensile direction.

Discussion

Zn–22Al alloy was modified with 2 % Cu to obtain the Zn–21Al–2Cu alloy named Zinalco alloy. Superplastic behavior of this alloy was evaluated in tension as function of temperature and strain rate. Maximum strain attainable in this alloy was found to depend strongly on the initial strain rate and testing temperature as shown in Fig. 2a for fine-grained microstructures of 1 µm of grain size (Fig. 1a).

This kind of dependence is in agreement with those reported for the Zn-22Al alloy [1–10], however, addition of the 2 % Cu decrease maximum strain attainable about 1800 %. The low strains observed in the Zinalco alloy is attributed to the formation of sharp necks and their subsequent growth within the gage length, as can be seen in Fig. 3a, b.

It is known that growing of macroscopic necks within gauge length depends on strain rate sensitivity parameter *(m)* [11, 23]. For most materials including Zn–22Al alloy, values of m higher than 0.3 are needed to maintain diffuse the necking. Under these conditions, necking areas can be deformed with approximately the same strain rate that the rest of the specimen and therefore, a stable superplastic flow can be reached [11, 23]. For Zn-22Al alloy the value of *m* is between 0.4 and 0.5. It is consistent with the observation of stable strains up to at least 800 % [11]. The value de *m* calculated for Zinalco alloy was 0.26, which indicates that additions of 2 % Cu in Zn-22Al alloy causes a decrease in the strain rate sensitivity. The value of *m* found in Zinalco alloy correspond with an early development of plastic flow instability observed in specimens of this alloy tested at several conditions of deformation (Fig. 3a, b). The low value of the strain rate sensitivity parameter in Zinalco alloy could be result of a hardening effect caused by the presence of copper in the alloy. This hardening effect is higher at low strain rates (10^{-3} s^{-1}), where values of flow stress in the Zn–21Al–2Cu alloy increase up to 600 % compared with those reported in Zn–22Al alloy [1–10].

Lower values of *m* can be related with the necking appearance, particularly with the degree of sharpness. However, further experiments will be necessary to investigate the effects the addition of 2 % Cu on flow localization and microstructural necking characteristics in Zn–22Al alloy.

From the results showed in Figs. 4 and 5, it can be noticed that addition of 2 % Cu in Zn–22Al alloy does not have a significant effect on grain size sensitivity (*p*), true activation energy (Q_t) and constant *A*. The values of this parameters were essentially similar to those reported for the Zn–22Al alloy [6, 7, 9, 10, 22] and for the Zn–22Al alloy doped with 0.13 wt% and 0.5 wt% Cu [18, 19].

Therefore, for Zinalco alloy the values found for parameters p, Q and A in Eq. 1 indicates that, in steady-state, grain boundary sliding (GBS) is the principal deformation mode for this alloy. The high value of the stress exponent *n* could result from a strain-enhanced grain growth during first stage of deformation process, as proposed by Caceres and Wilkinson [18], who suggested that the primary role of the Cu in a Zn–22Al–0.5Cu alloy is to influence grain growth. This observation is supported by the changes observed on the microstructure of Fig. 6, which shows an increase in the grain size of α and η as a result of deformation at 513 K and 10^{-3} s^{-1} (compare Figs. 1a and 6). A deeper analysis is needed to establish the role of this alloying element on grain growth of the alloy above mentioned. Finally, it is important to note that η phase show substantial elongation capacity when Zinalco alloy is deformed at 513 K and 10^{-3} s^{-1} (see Fig. 6). It seems to be related with a large-deformation capability observed after beginning of plastic flow instability (Fig. 3b, letter E).

Conclusions

The main conclusions that can be extracted from this work are listed below:

(1) The maximum strain attainable in the Zn–21Al–2Cu alloy (Zinalco alloy) with a grain size of about 1 μm, depends strongly on the initial strain rate and testing temperature. Highest elongation to fracture was obtained when the tensile deformation is carried out at 513 K and 10^{-3} s^{-1}.

(2) An addition of 2 % Cu in the Zn–22Al alloy results in a reduction of the maximum strain attainable, and in a shift of this maximum to lower strain rates. Presence of Cu also results in an increase of flow stress, particularly at low strain rates, which results in lower strain rate sensitivity.

(3) Presence of 2 % Cu in Zn-22Al alloy causes an increase of the stress exponent (*n*) from 2.5 to approximately 3.9. In contrast, the values of grain size sensitivity (*p*), true activation energy (*Qt*) and constant A of the constitutive equation has not significant changes.

(4) The main effect of Cu (2 %) in the Zn–22Al alloy is to produce an early development of the superplastic flow instability. For Zn–21Al–2Cu alloy, this instability was characterized by the formation of sharp necks and their growth as a result of the decrease in the strain rate sensitivity. This low value of m can be explained as consequence of a hardening effect at low strain rates originated by the presence of Cu in the alloy.

(5) In the Zn-21Al-2Cu alloy deformed at 513 K and 10^{-3} s^{-1}, was observed a substantial elongation capability of the η phase which could be the responsible of the large deformations observed after beginning of plastic flow instability.

Acknowledgements The authors of the present work would like to acknowledge the financial support for the project C10-FAI-05-04.67 and the facilities provided at CCIM-UASLP to perform the experiments. We also thank Dr. Jesus Negrete Sanchez for his collaboration in this investigation and Emmanuel Gutierrez, Minerva Aranda, Margarita Alvarez, and Alfredo Ruiz for their technical assistance.

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