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FORMER β BOUNDARIES CHARACTERIZATION IN THE SUPERPLASTIC MICROSTRUCTURE OF A Zn-Al EUTECTOID ALLOY MODIFIED WITH 2%Wt OF Cu

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ABSTRACT

The effect of three different solutionizing and annealing heat treatments on the initial superplastic microstructure of a Zn-21Al-2Cu alloy was studied. Microstructural characterization using SEM and DRX techniques revels the presence of residual grain boundaries of a high temperature β phase (referred to as Former β Boundaries, FβBs) which encompass groups of fine α (Al rich phase) and η (Zn rich phase). The origin of these arrangements may most likely be due to small deviations from the eutectoid composition as consequence of the Cu addition, which preferentially promotes the precipitation of proeutectoid phase to the high temperature phase boundaries. The final domains size only are influenced by the solutionizing treatment time, while the fine phases size only is affected by the duration of the subsequent annealing process. The presence and characteristic of his FβBs could be import in order to explain possible microstructural changes, which lead to a reduction of the grain boundary sliding capacities of fine α, and η phases that conduces at the early onset of a non-stable plastic flow previously observed in this alloy.

Keywords: Microstructural Characterization; Superplasticity; Zn-Al-Cu alloys.

INTRODUCTION

In metal alloys, generally with eutectoid composition, has been observed the phenomenon of superplasticity, which refers to the ability to exhibit large and homogeneous plastic elongations (usually greater than 500%) when are pull in tension at strain rate (ε) in the interval from 10^{-5} to 10^{-2} s^{-1} and temperatures above 0.5Tf (Tf is the melting point in K) [1-4]. In order to achieve superplastic flow, the microstructure must have a fine equiaxed grain size (<10 μm) [1-2, 4]. In alloys with eutectoid composition, it is possible to obtain a fine microstructure if the alloy is suddenly cooled after a solutionizing treatment above eutectoid temperature. This procedure promotes the decomposition of high temperature phase in a fine two-phase mixture, where the presence of a second phase helps to stabilize the grain size. The fine microduplex microstructure generally is subject to a posterior annealing for the grain size stabilization.

One of the superplastic alloys whose behavior has been studied extensively is the eutectic Zn-22Al [5-6]. In this alloy microstructural characterization has been showed that the initial fine microstructure remain without appreciable changes after the superplastic deformation and this fact has served to establish that the deformation is carried out mainly by the movement of grains in response to applied stress by a mechanism of Grain Boundary Sliding (GBS) [7]. In this alloy also some kind of microstructural rearrangements characterized by the presence of residual grain boundaries of the high temperature phase, which serve as microestructural tracers, has been reported as function of the type and level of impurities [8-9]. The characteristics of these microstructural arrangements, which are function of the conditions used in the solutionizing treatment above the eutectoid temperature, seems to be important in the superplastic deformation process for this alloy [8-9]. Particularly the presence of this kind of microstructural rearrangements was used to explain the formation of cavity stringers, which are formed by the operation of this residual boundaries as obstacles to the sliding of the either individual fine grains of phases rich in Zn an Al, in the Zn-22Al alloy doped with Cu and Fe [10].

By other hand, in the eutectoid Zn-22Al alloy have been achieved tensile elongations close to 3000%, however, because had poor mechanical properties, industrial application is limited. The alloy Zn-21Al-2Cu, resulting from the addition of 2%wt. copper to the eutectic Zn-22Al [11], has good mechanical and corrosion properties, which allowed the application of this alloy in industrial processes [11]. As part of a series of studies aimed to evaluating the Zn-21Al-2Cu alloy as possible material for superplastic forming operations, in the present investigation, microstructural characterization of specimens with different solutionizing heat treatment was carried out. The presence and characteristics of similar microstructural arrangements as those observed in the eutectoid Zn-22Al alloy was evaluated in order to obtain information about the effect of the copper additions higher as 2% on the characteristics of these arrangements.

MATERIALS AND METHODS

The Zn-21Al-2Cu alloy used in the present investigation was prepared using high purity Zn, Al and Cu elements. After melting process, the alloy was solidified by a continuous casting process to obtain a cylindrical rod which was extruded at 290ºC. Profiles obtained with a thickness of 5 mm were then rolled at 240°C to a thickness of 2.5 mm. From these sheets were obtained specimens, which were subjected to three different heat treatments to obtain a fine-grained microstructure.

Based on researches about the superplasticity phenomenon in Zn-22Al alloys [5-6], the first treatment proposed consisted of a solutionizing heat treated for 15 hrs at 360ºC followed by rapid quenching in ice water and subsequent annealing for 5 hrs at 250°C. In order to investigate a possibility to reduce energy costs, a second treatment was proposed. In this treatment the annealing process was avoided and the specimens only were solutionizing heat treated for 1 hr at 350°C followed by a rapid quenching. Finally, the effect of a prolonged annealing process on the microstructure was investigated. In this third propose, samples were annealed 91 hrs at 250°C after an initial heat treatment similar as described in the second propose. After heat treatments, the specimens were metallographically polished down with diamond paste of 3 and 0.5 μm. Scanning Electron Microscopy (SEM) and X-Ray Diffraction (XRD) techniques was used to characterize the microstructure in the specimens. The XRD diffractograms obtained were refined by the Ritveld method using the MAUD software.

RESULTS AND DISCUSSION

In Zn-22Al-2Cu alloy a fine mixture of Zn and Al rich phases results of the recently proposed phase transformation to the system Zn-Al with compositions close to the eutectoid:

β(triclinic) $\longrightarrow$ η (hcp) phase + R (rhombohedral).

Where R is a phase transition that transforms in the phases mixture: η (hcp) + α (fcc), which are Zn and Al rich phases, respectively [12].

The size and shape of final microstructure will depend of the quenching rate and as well as the time and temperature used during the solutionizing and annealing process. In this investigation, the effect of three different heat treatments on the Zn-21Al-2Cu alloy microstructure was studied. It was observed that all treatments results in formation of a homogeneous microstructure (Figures 1a-1c) consisting of groups of fine η and α grains that seems to be surrounded by residual boundaries of β high temperature phase (letter A in Figures 1a-1c), which divide the microstructure into equiaxed domains. These residual boundaries seem to be formed mainly by elongated grains of α phase, however is import to note that these dominions are incomplete in the major of cases. The presence of η and α phases in all microstructures was confirmed by XRD analyses. From the diffractogram shown in Figure 1d, which corresponding to the microstructure of Figure 1a, it can be seen that in addition to these phases exist a small peak corresponding to the stable phase τ', (Al_4Cu_3Zn), which corresponding to a gray grains in Figure 1a.

The microstructural arrangements founded in Zn-21Al-2Cu alloy are similar to those previously reported in Zn-22Al alloy, where similar boundaries are referred to as former α boundaries (FαBs) [8-9]. Due to this similitude in this work the boundaries observed in Figures1a-c will be named Former Beta Boundaries (FβBs). A close inspection of Figures 1a-c reveals differences in domains size and in the size of the fine phases that they contain as function of the heat treatment used. It was observed that final size of these domains are only influenced by the time period for the solutionizing heat treatment, while the duration of the subsequent annealing process only affect the size of fine phases contained in the interior of FβBs. This kind of dependence also has been reported in the Zn-22Al alloy [8-9], however unlike Zn-22Al alloy, in Zn-21Al-2Cu alloy the amount of Cu present (2%wt), significantly reduces the size of these domains but does not appear to affect the size of the fine phases. These characteristics are shown in Table 1, which presents the results of measurements made on the domains and fine grains observed in Figures 1a-c using the mean linear method. Corresponding measurements reported for the pure Zn-22Al alloy [8] and Zn-22Al doped with Cu [13] also are given in Table 1 for comparison.

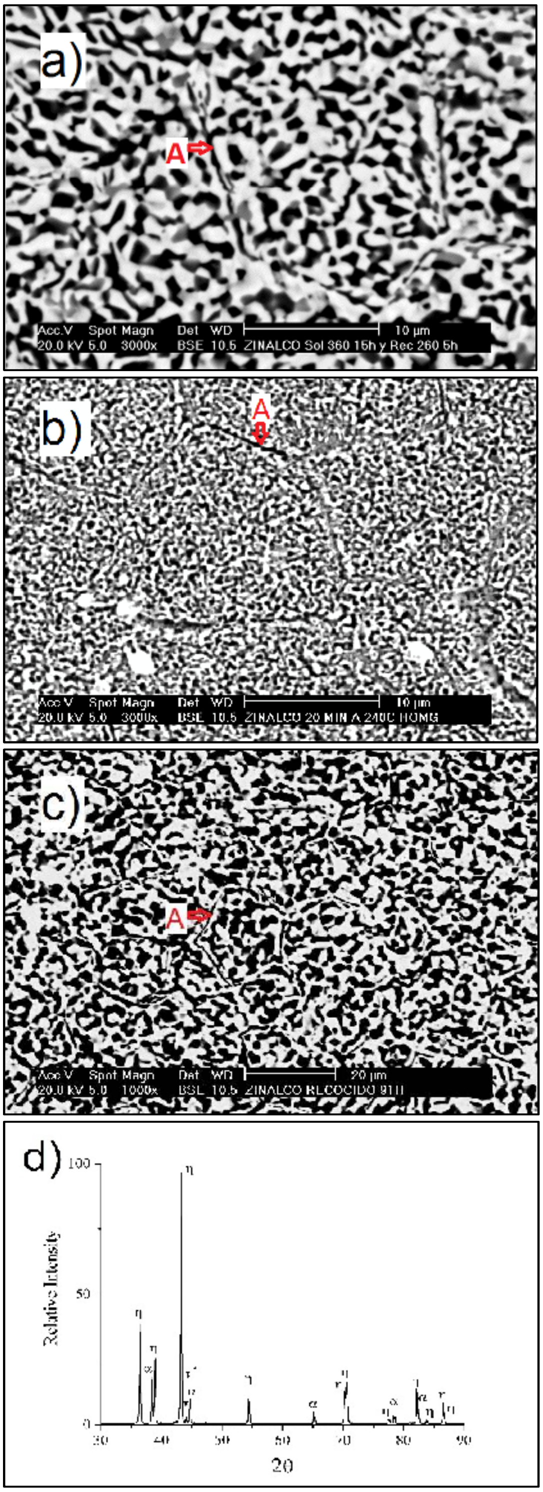

Fig. 1. Microstructure in Zn-21Al-2Cu alloy after different heat treatments show presence a fine mixture of α and η phases enclosed by residual boundaries of the high temperature β phase (letter A). (a) Solutionizing by 15 hrs at 633K + Quenching + Annealing by 5 hrs at 533K , (b) Solutionizing by 1 hrs at 623K + Quenching, (c) Solutionizing by 1 hr at 633K + Quenching + Annealing by 91 hrs at 523K and (d) DRX spectrum from Fig1a that show presence of α, η and τ´ phases.

Using the measurements of the Table 1, the effect of the annealing time at 250°C on the grain size for the fine microstructure in Zn-21Al-2Cu alloy, was evaluated and the results are shown in Figure 2. The grain growth in metals and alloys can be described approximately by the expression: $d = Kt^n$, where d is the grain size, t is the time, K is a constant and n is the grain growth exponent

Table 1. Comparative average sizes of domains and fine phases as function of different heat treatments applied on Zn-21Al-2Cu, Zn-22Al and Zn-22Al doped with Cu alloys.

Alloy	Heat Treatment	Domains Average Size (µm)	Fine phases Average Size (µm)
Zn-21Al-2Cu	Solutionizing by 1 hr at 350ºC + Quenching	16	0.85
Zn-21Al-2Cu	Solutionizing by 1 hr at 350ºC + Quenching + Annealing by 91 hrs at 250ºC	18	4.5
Zn-21Al-2Cu	Solutionizing by 15 hrs at 360ºC + Quenching + Annealing by 5 hrs at 260ºC	40	2.35
High Purity Zn-22Al [8]	Solutionizing by 15 hr at 350ºC + Quenching + Annealing by 10 hrs at 260ºC	1000	2.5
High Purity Zn-22Al [8]	Solutionizing by 1 hr at 350ºC + Quenching + Annealing by 10 hrs at 260ºC	350	2.5
Zn-22Al Doped with Cu [13]	Solutionizing by 15 hr at 350ºC + Quenching + Annealing by 10 hrs at 260ºC	850	2.5
Zn-22Al Doped with Cu [13]	Solutionizing by 1 hr at 350ºC + Quenching + Annealing by 10 hrs at 260ºC	300	2.5

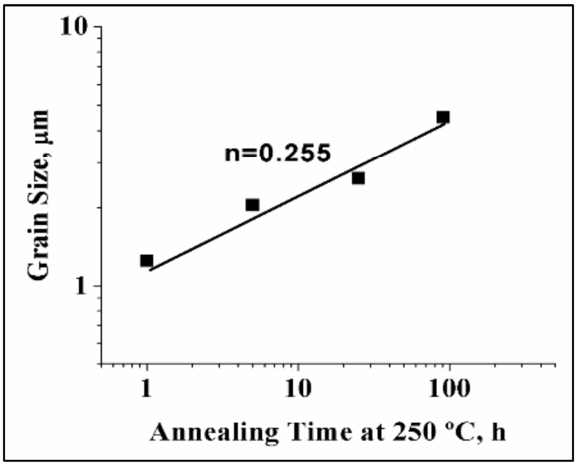

Fig. 2. Grain size of the Zn-21Al-2Cu alloy as function of the annealing time to the determination of the grain growth exponent (n).

From the slope in Figure 2, a value of n =0.255 was calculated for the Zn-21Al-2Cu alloy. This value is close to the calculated for the Zn-22Al alloy (0.27) [8]. These results confirm that Cu amounts higher as 2%wt does not affect the growth kinetics of both α and η phases and therefore the Cu has little tendency to segregate towards the grain boundaries in both phases.

The possibility that metal alloys exhibit superplastic behavior mainly depends on the fact that the microstructure is composed by fine and equiaxed grains [1-2, 4]. Therefore, heat treatment plays an important role in order to obtain conditions for the superplastic deformation of these alloys. For the Zn-22Al-2Cu alloy the micrographs in Figures 1a-c, correspond at the three treatment studied, show that in all cases the microstructure consisting of regions composed by a mixture of very fine grains of α (phase rich in Al) and η (Zn-rich phase) phases, which in addition are in some regions delimited by residual boundaries of the β high temperature phase, named Former β Boundaries (FβBs). This kind of microstructural arrangement has been reported early in different grades of Zn-22Al alloy [8, 14].

It has been suggested that the presence of these arrangements may most likely be due to small deviations from the eutectoid composition that promotes the precipitation of proeutectoid phase to the boundaries of the high temperature phase [8], which leads to the formation of similar boundaries to those allotriomorphs boundaries found in hipoeutectoid steels [15]. In Zn-22Al-2Cu alloy, the origin of the microstructural arrangements observed in Figures 1a-1c is attributed to the compositional deviation caused by the addition of 2% Cu at eutectoid Zn-Al alloy.

The domains size encompasses by the FβBs observed is proportional to the heat solutionizing time. In Zn-22Al alloy this kind of dependence was also established [8-9]. However, unlike the observations made in the Zn-22Al alloy, it was observed that the presence of Cu decreases the size of the FβBs from 350μm to 20μm in similar conditions of heat treatment. This can be expected considering the observations made in pure Zn-22Al, Zn-22Al doped with Cu and Zn-22Al doped with Fe, which indicates that the size of the domains is influenced by the amount and type of chemical elements added to the eutectoid composition [8]. In Zn-22Al-2Cu alloy the size of FβBs observed indicates that the addition of 2%wt Cu refine the size of the high temperature phase. This suggests that the presence of Cu helps to create more number of sites for the β phase grains nucleation during the heat solutionizing treatment resulting in a fine grain size of this phase.

A close inspection of the Figure 1a-1c also show that the majority of the FβBs obtained by the heat treatment are composed by continuous sections of elongated α phase and discontinuous sections formed by fine grains of α and η phases. These observations are not consist with those reported in the Zn-22Al alloy, where was observed that these borders are completely formed by elongated grains of α phase [8-9]. Based in previous observations made in Zn-22Al alloy, where the fine grains domains defined by the complete FαBs behave as a unit during the superplastic deformation [9], it is expected that in Zn-21Al-2Cu alloy as a consequence of the superplastic deformation, the FβBs tend to broke. This behavior probably convert at these broken sections of the FβBs in obstacles which difficult and delay the sliding of the fine grains when the deformation increases. This suggestion could be explain the alignment process of the fine microstructure that has been reported in the Zn-21Al-2Cu alloy [15] and which has been connected recently with the onset of the plastic instability in this alloy [16].

CONCLUSIONS

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

1. In the Zn-21Al-2Cu alloy, after the heat treatment which produce a fine grained microstructure, exist the presence of microstructural arrangements consisting of residual grain boundaries of a high temperature β phase which encompass domains of fine α (Al rich phase) and η (Zn rich phase).
2. The origin of these residual grain boundaries is attributed to the compositional deviation caused by the addition of 2% Cu at eutectoid Zn-Al alloy, which preferentially promotes the precipitation of proeutectoid phase to the high temperature phase boundaries.
3. The 2% Cu addition in the eutectoid Zn-Al alloy, lead to increase the number of sites for the high temperature phase grains nucleation during the heat solutionizing treatment, resulting in a fine grain size of this phase.
4. The final domains size only are influenced by the solutionizing treatment time, while the fine α and η phases size only is affect by the duration of the subsequent annealing process.

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