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## Original Article

# Evaluation of hardening and softening behaviors in Zn–21Al–2Cu alloy processed by equal channel angular pressing<sup>☆</sup>



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## ABSTRACT

The microstructural evolution of as-cast and homogenized Zn–21Al–2Cu samples after two and six passes in an equal channel angular pressing (ECAP) at room temperature was reported. A homogenization treatment for 24 h at 350 °C was applied to the as-cast samples followed by deformation. An annealing heat treatment was performed on all samples after the ECAP process. Our results showed that the homogenized and deformed samples displayed a uniform fine-grained microstructure after annealing, while as-cast samples without homogenization treatment presented only some regions of fine-grained microstructure. The level of microsegregation was higher in the as-cast samples as compared to the homogenized ones even after annealing. Vickers microhardness measurement on samples after deformation is smaller than the original material indicating a softening. However, after the annealing treatment, the microhardness increased, indicating that there was a slight hardening of the material.

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## 1. Introduction

The Zn–Al eutectoid alloy has been extensively studied as it has a low melting point, good castability, favorable wear

resistance, low forming temperature, high strain rate sensitivity, and high plastic deformability due to the superplasticity phenomenon it presents [1,2]. This alloy forms a lamellar microstructure during solidification requiring stages of plastic deformation and annealing treatments to form a fine,

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equiaxed-grained microstructure [2,3]. Numerous thermo-mechanical treatments have been proposed for obtaining the fine-grained microstructure required for the superplastic deformation of Zn–Al eutectoid alloy. Most of these treatments involve first homogenizing the as-cast alloy, followed by multistage rolling [3] or extruding [2], and then different annealing treatments. Tanaka et al. [4] reported a minimum grain size of 0.35  $\mu\text{m}$  when a Zn–22Al alloy was subjected to four passes of ECAP at room temperature after the alloy had been quenched from 350 °C. Yang et al. [5] found an average grain size of 0.3, 0.5 and 0.8  $\mu\text{m}$  when a microduplex alloy Zn–22Al was subjected to eight passes of ECAP at –10, 25 and 50 °C, respectively. One of the main conclusions of their work was that the grain refinement was attributed to the dynamic recrystallization of the Zn-rich phase. In addition, it has been proposed that this alloy can exhibit high strain rate superplasticity due to this significant refinement. Kawasaki et al. [6] reported a reduction in the average grain size from 1.8 to 0.8  $\mu\text{m}$  in the same alloy but processed with eight passes of ECAP at 200 °C. These authors argued that the ECAP processing produces larger agglomerates of grains with interfaces of the Al–Al type (as compared to conventionally processed superplastic alloy), which in turn inhibits superplastic behavior. In other research, Demirtas et al. [7] reported that the average grain size of the Zn–22Al alloy had reached 200 nm, the lowest size reported so far for this alloy. They claimed that it was possible to achieve such a low grain size thanks to a two-step ECAP process, where up to four passes at 350 °C were applied first, followed by another four passes applied at room temperature. They also report that almost half of the grains presented an aspect ratio close to 1 for both phases. In a very recent report, Demirtas et al. [8] studied the ability to achieve ultrafine grain sizes with several conventional thermomechanical processing routes and ECAP processes. They found that while some conventional thermo-mechanical processes produced finer, average grain sizes in comparison to ECAP processing, some lamellar areas were preserved in the former processes while the latter exhibited a lamellar-free microstructure. On the other hand, an atypical phenomenon has been observed in Zn–Al eutectoid alloy as well as alloys modified with 0.3 and 2 wt% of Cu, this phenomenon consists of a work-softening and anneal-hardening of these alloys [2,3,9]. For potential applications, it is of interest to find processes that produce a fine grain microstructure, especially for as-cast alloy, with fewer processing steps. The aim of this work is to study the effect of equal channel angular pressing (ECAP) on the microstructure of Zn–22Al–2Cu. We assessed whether this alloy shows the work-softening and

anneal-hardening effects observed for conventional thermo-mechanical processes involving rolling and extrusion. The results are compared with those obtained by Yang et al. [3] for the Zn–Al eutectoid alloy and the eutectoid modified with 0.3 wt% of Cu. This work was focused on reporting the effect of copper content on the atypical behavior of these alloys and the advantages of processing by ECAP for obtaining a fine-grained microstructure.

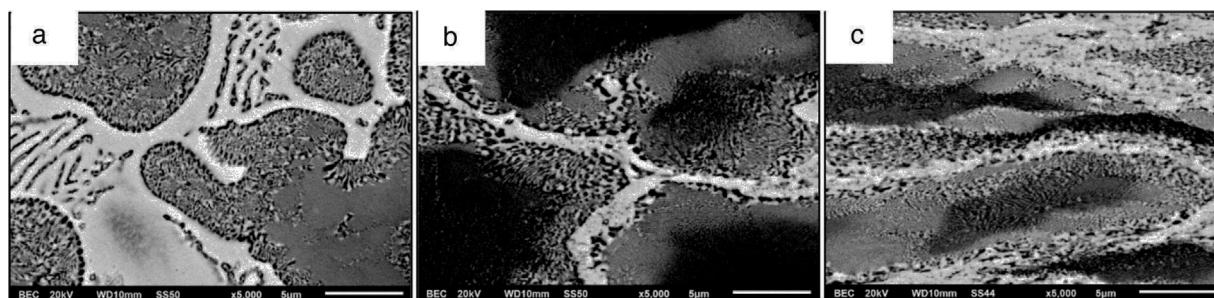
## 2. Experimental procedure

An induction furnace was used to produce the Zn–21Al–2Cu alloy by melting proper amounts of Zn (99.99%), Al (99.99%), and Cu (99.96%). The alloy was melted in a graphite crucible exposed to air and poured into cylindrical bars of 19 mm in diameter and 35 mm in length. After that, some bars were homogenized at 350 °C for 24 h in air. Cast and homogenized samples were subjected to an equal channel angular extrusion (ECAP) in a die with two cylindrical channels with a diameter of 15.8 mm. The inner intersecting angle ( $\varphi$ ) was 90° and the outer angle ( $\psi$ ) was 36°. All samples were extruded by two and six passes with a ram velocity of 5 mm/min and by using  $B_c$  route. The lubricant used was MoS<sub>2</sub> and it was applied to both channels on each pass. The process was carried out in a universal testing machine Shimadzu AG-I set to 600 kN at room temperature. Then, deformed samples were annealed at 270 °C for 30 and 120 min. Longitudinal sections of annealed and deformed samples were ground and polished in order to characterize their microstructure using a JEOL 6610 LV scanning electron microscope. Vickers microhardness was evaluated in a Shimadzu HMV-G21DT microhardness-testing machine using a load of 1.96 N applied for 15 s. At least 8 values were taken for each specimen to obtain an average.

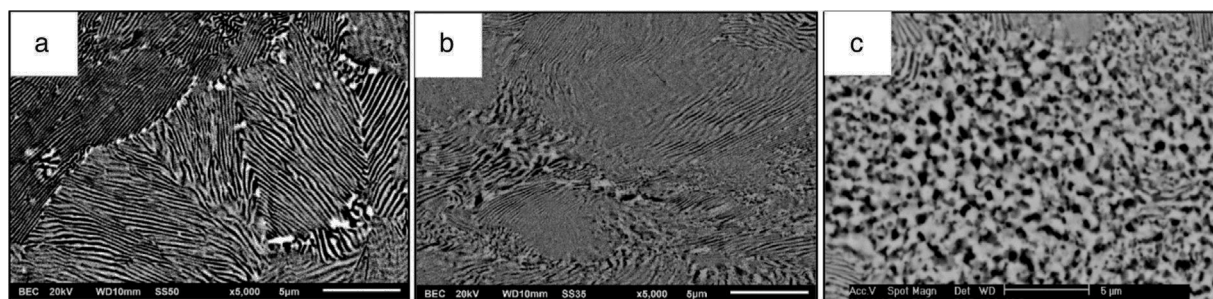
## 3. Results and discussion

### 3.1. Effect of SPD on microstructure and microhardness

Fig. 1 exhibits the cast microstructure at high magnification. In Fig. 1a, the dendritic pattern composed of the zinc-rich phase ( $\eta$ ) and aluminum rich phase ( $\alpha$ ) can be seen. The former can be seen in a bright contrast and the latter in a gray contrast. In addition, the two zones (with lamellar and granular morphology) produced by the eutectoid reaction surrounded by the  $\eta$  phase can be distinguished. Fig. 1b shows the same



**Fig. 1** – SEM micrographs of the samples with initial cast morphology (a) without deformation, (b) with two passes, and (c) with six passes.

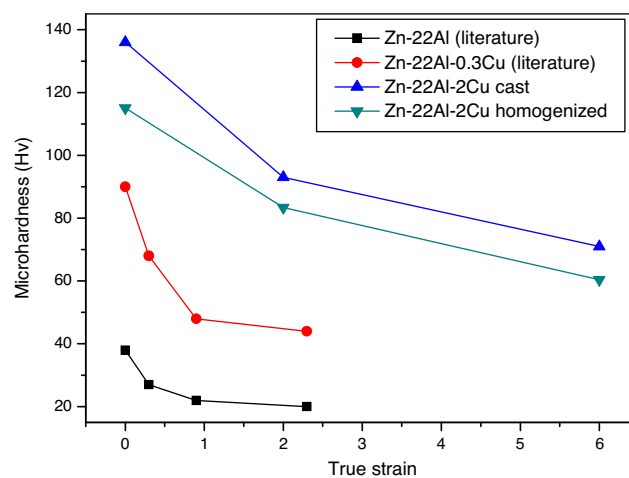


**Fig. 2 – SEM micrographs at a high magnification of the samples with homogenized morphology (a) without deformation, (b) with two passes, and (c) with six passes.**

dendritic pattern with some preferential orientation visible from left to right, which can be attributed to the two passes of ECAP that were applied to this sample. In Fig. 1c, it can be noted that the deformation pattern is more accentuated in the microstructure. However, the level of microsegregation is still very significant. It is also evident that the bright and gray areas exhibit a partial fine-grained morphology. This change can be attributed to a combination of two mechanisms: a mechanical twist effect of the  $\alpha$  phase and a dynamic recrystallization of  $\eta$  phase [3]. Fig. 2 shows the homogenized microstructure of the samples. It can be noted (inset 2a) that a lamellar morphology has been obtained. In inset 2b, the microstructure corresponding to two passes of ECAP is shown. The micrograph displays how the lamellar microstructure is now distorted because of the application of the severe deformation. In some areas, the initial morphology is very clear. However, in other regions, the separation distance between the layers of both phases are no longer distinguishable, a result that is proposed as evidence of the mechanical twist effect caused by ECAP. A micrograph corresponding to six passes of ECAP is presented in Fig. 2c. As it can be seen, there are few areas of  $\eta$  phase which exhibit dendritic morphology, while the majority of the microstructure shows a fine granular morphology of  $\alpha$  and  $\eta$ . As it has already been mentioned, it is believed that this microstructure is the result of the mechanical twist effect of the aluminum-rich phase and the dynamic recrystallization of zinc-rich phase. Yang et al. [3] have demonstrated by means of DSC runs that the recrystallization temperature of the  $\alpha$  phase was 337 °C and the corresponding temperature of  $\eta$  phase was –12 °C. Consequently, it is proposed that the former phase is fractured and mixed along the microstructure while the latter experiences dynamic recrystallization during severe plastic deformation at room temperature. This is the best explanation for the fine microstructure shown in Fig. 2c. It is important to note that even for six passes, there are still some areas that retain a lamellar morphology due to the deformation heterogeneity as shown in Fig. 2c.

In this case, it may be necessary to subject the sample to longer homogenization treatments and/or more passes of ECAP in order to see if these areas disappeared with higher strain.

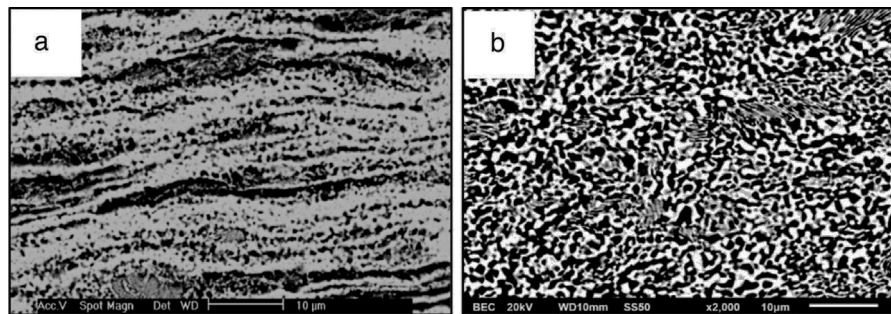
Fig. 3 displays the behavior of the microhardness of the cast and homogenized samples as they were subjected to several passes of ECAP. These are compared with results in



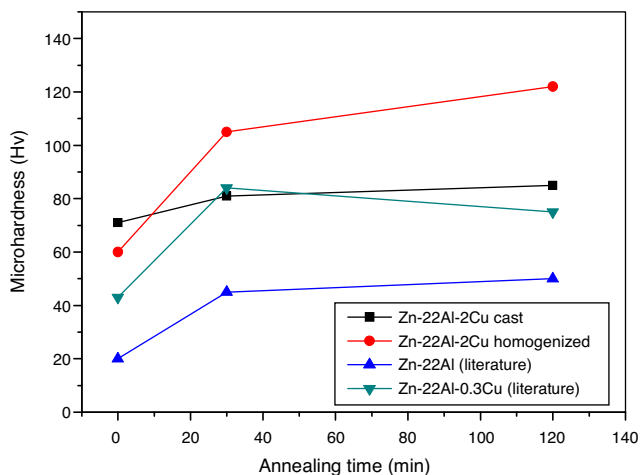
**Fig. 3 – Microhardness graph for the Zn–Al alloy studied in this work compared with values from the literature.**

the literature [3], where the microhardness values for Zn–22Al and Zn–22Al–0.3Cu alloys are reported for lower strain values. As it can be seen, the general tendency is for a decrease in the microhardness as the strain increases.

It is important to point out that this work has confirmed through experimentation that softening during deformation is still seen at higher strain values, in comparison to the previously published results. It is also important to mention that the Cu content has a significant effect on the hardness of the alloy since our values are higher in both the cast and homogenized samples, compared to the ones previously reported [3]. The general phenomenon observed for the microhardness of the deformed samples supports the hypothesis concerning the recrystallization of the Zn-rich phase during the ECAP process. It is proposed that the higher hardness values exhibited for the cast specimens are due to the presence of higher microsegregation in comparison with the homogenized samples. El-Danaf et al. [10] have recently reported a similar work-softening phenomenon in a eutectic Pb–Sn alloy subjected to ECAP processing. They concluded that a combination of eutectic crystals fracturing and recrystallization of  $\alpha$  and  $\beta$  phases leads to a change in morphology from lamellar to fine grains after four passes.



**Fig. 4** – SEM micrographs of the cast samples subjected to six passes of ECAP for (a) 30 min and (b) 120 min of annealing at 275 °C.



**Fig. 5** – Comparison of the hardness behavior seen in the experimental samples influenced by the annealing time and previously reported literature values.

### 3.2. Evolution of microstructure and microhardness during annealing

Fig. 4 shows the microstructure of cast and homogenized samples with six passes of ECAP when they are subjected to an annealing at 275 °C for 120 min. As it can be observed, the microsegregation level is still present throughout the entire sample (Fig. 4a). Although, it is also evident that there are some areas where there exists a fine-grained microstructure. The resultant microstructure seen in the homogenized sample processed with six passes of ECAP and annealed at 275 °C for the same time is shown in Fig. 4b. It is evident that the microstructure has fine grains with a size close to 1 µm and also very few zones with lamellar morphology remaining in the microstructure. Fig. 5 shows the microhardness behavior of the cast and homogenized samples (with six passes of ECAP) annealed at 275 °C for 30 and 120 min. These results are compared to those previously published [3]. It can be noted that the hardness increases in both samples as the annealing time is increased. However, the increment is significantly higher in the case of the homogenized sample in comparison to the cast one. This result can be attributed to the initial morphology. We have already demonstrated that even for six passes of ECAP,

the cast sample possesses a mixed morphology of dendritic and granular arrays and an evident level of microsegregation, while the homogenized sample shows fine grain morphology with some isolated islands of lamellar microstructure. According to a previous report [3], longer annealing times lead to an increase in the quantity of high angle boundaries in the microstructure, which in turn leads to the reduction of heterogeneous nucleation sites of dynamic recovery which causes the observed hardening.

In our case, we proposed that the increase in the relative amount of high angle boundaries is higher in the homogenized sample than the as-cast sample. However, a more in-depth study quantifying this parameter by electron backscatter diffraction is being carried out at present. Zhang et al. [2] have associated this anneal-hardening phenomenon to phase transformation of the suspensive zinc-rich phase ( $\alpha_2$ ) to the harder equilibrium Al-rich  $\alpha_1$  and the zinc-rich  $\eta$  phases. However, it should be noted that this mechanism is not relevant to the system we studied, as the formation of suspensive  $\alpha_2$  phase is improbable during the slow cooling conditions that prevail throughout the cast and homogenization processes.

## 4. Conclusions

It was demonstrated that work softening in a Zn-21Al-2Cu alloy is valid even for true strains close to 6 in both cast and homogenized samples.

It was found that homogenized samples displayed a fine grain microstructure (size less than 1 µm), while in the case of the cast samples, the microsegregation pattern and zones with initial dendritic microstructure remained evident after six passes of ECAP.

It was found that during the annealing of the cast and homogenized samples with six passes of ECAP, there was an anneal-hardening phenomenon which was attributed to an increase in the relative amount of high angle grain boundaries in both samples. However, it was observed that this increase was more significant in the case of the homogenized samples.

## Conflicts of interest

The authors declare no conflicts of interest.

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