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Mechanical Alloying and Milling of Zn-Rich Zn-Al-Cu Alloys

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Abstract. The objective of this study is to analyze the microstructural evolution and phase transformations that take place during the mechanical milling of a Zn-22wt.%Al-2wt.% Cu alloy powder and mechanical alloying of Zn-22wt.%Al-2wt.%Cu, Zn-20wt.%Al-10wt.%Cu and Zn-10wt.%Al-22wt.%Cu elemental powder mixtures. The milling procedure was carried out under an argon atmosphere using a horizontal stainless steel mill with balls of same material (ball to sample weight ratio of 36:1). Powder mixtures were prepared from pure metal powders and Zn-22wt.%Al-2wt.% Cu alloy fillings were prepared by machining of a furnace-cooled alloy. Milled powders were analyzed by X-ray diffraction, scanning electron microscope and transmission electron microscope. XRD results of mechanically alloyed Zn-Al-Cu alloys showed that the (Al-rich) α, (Zn-rich) η and ($CuZn_4$) ε phases were formed at the beginning of milling. No solubility extension was observed in both α and η phases. The appearance of (110) peak diffraction of τ' phase along the decrease of intensity of ε phase diffraction peaks was observed for longer millings. This suggests that the following four-phase reaction took place: $\alpha + \varepsilon \rightarrow \eta + \tau'$. Similar results were observed in mechanically milled Zn-22wt.%-2wt.%Cu alloy, which presented a mixture of α, η and ε phases before milling. Besides, it was noticed that the η phase decomposed into a Zn-richer η phase due to the shift of (0002) diffraction peak. The equilibrium α, η and τ' phases were present in both mechanically alloyed and milled samples after 1080 ks of milling. SEM observation of mechanically milled samples showed that the eutectoid lamellar microstructure of Zn-22wt.%Al-2wt.% Cu alloy is transformed to a microstructure of fine α phase particles dispersed in the η phase matrix. TEM observation of both mechanically alloyed and milled powders indicated that the equilibrium phases presented a size of 50-100 nm.

Introduction

The mechanical alloying (MA) process has been applied widely to produce alloys in binary systems, enabling us to obtain intermetallic compounds, supersaturated solid solutions and also amorphous alloys [1]. These alloys have the characteristic of forming nanostructures, which are expected to attribute better physicochemical properties to these alloys [2]. However, the processing of ternary alloys by MA has not been widely studied, compared to binary alloys. Thus, a study of mechanical alloying in ternary systems is important to clarify the alloying mechanism and to find new alloys with better physical properties. Besides, it has been reported [3] that several phase transformations can be induced by the plastic deformation during tension test of an eutectoid Zn-22wt.%Al-2wt.%Cu alloy. Thus, the mechanical milling (MM) of alloy powders could be a good alternative to follow the phase transformations that take place by plastic deformation during the milling of Zn-Al-Cu alloys. Additionally, we have not found any previous report on mechanical alloying and milling in the Zn-Al-Cu system. Therefore, the purpose of this work is to study the phase formation and microstructure evolution in Zn-rich Zn-Al-Cu alloys

Experimental Procedure

The following elemental powder mixtures Zn-22wt.%Al-2wt.%Cu , Zn-20wt.%Al-10wt.%Cu and Zn-10%wt.Al-22wt.%Cu were prepared using pure metallic powders. Besides, an ingot of Zn-22wt.%Al-2wt.%Cu was solution treated at 350 °C for 4 days, and then furnace-cooled (FC) to room temperature. Alloy fillings were prepared by machining using water cooling. Both alloy fillings and powder mixtures were placed into an austenitic stainless steel vial. Methanol was used as surfactant agent. Austenitic stainless balls of 12 mm diameter were used for milling with a ball to powder weight ratio of 36:1. The milling was carried out under an argon gas atmosphere and at a rotation speed of about 110 r.p.m. A small amount of sample was taken at specific milling times, keeping the weight ratio of 36:1. These samples were analyzed by X-ray diffraction, scanning electron microscopy and transmission electron microscopy.
The X-ray diffraction analysis was conducted in a diffractometer, using Cu Kα radiation filtered with nickel and a scanning rate was 1 degree per minute. The mechanically alloyed and milled powders were cold consolidated to obtain a cylindrical sample of 10 mm diameter and 10 mm high, using a hydraulic press machine with 2 tons. These samples were mounted on epoxy resin to be prepared metalographically with 0.05 μm alumina and observed with backscattered electrons at 20 kV in a scanning electron microscope. The milled powders were also mounted on a carbon-coated copper-grit of 3 mm diameter and then observed at 200 kV in a transmission electron microscope.

Results and Discussion

X-Ray Diffraction Analysis of Mechanically Alloyed and Milled Powders. Figure 1(a) corresponds to the X-ray diffraction (XRD) pattern of the Zn-22wt.%Al-2wt.%Cu powder mixture milled for 0, 180, 360, 540 and 1080 ks. The XRD pattern of powder mixture without milling presents diffraction peaks corresponding to the pure elemental components. The sequence of diffractograms with milling time makes evident the disappearance of the copper diffraction peak. It can be also observed that the Zn (0002) diffraction peak is shifted slightly to higher 2θ angles. This means that the lattice parameter c decreased from 0.494 nm to 0.492 nm. This is in agreement with the reported values of c for the η phase, 0.487- 0.494 nm [2]. On the other hand, it can be observed that the Al (200) diffraction peak is also shifted slightly to higher 2θ angles, decreasing its lattice parameter, a, from 0.4046 to 0.4042 nm. This small change in both lattice parameters suggests the formation of α and η phases during milling. It is important to say that according to the values of lattice parameter, it was not achieved an increase of solubility of aluminum in zinc or viceversa, as reported in several immiscible binary alloys obtained by mechanical alloying [1]. The chemical analysis of milled powders showed a very small content of iron and thus we believe that there is no effect of impurities on the phase transformations of these alloys. It can be also noticed an increase of the width of diffraction peaks at high 2θ angles increases with milling time, which is mainly attributed to the formation of a nanometer grain size [1]. The XRD pattern of powder mixture milled for 1080 ks shows the formation of τ', α and η phases. In order to analyze the formation of τ' phase, the copper content of powder mixture was increased. The XRD patterns of Zn-20wt.%Al-10wt.%Cu powder mixture milled for different times are shown in Fig. 1 (b). Here, it is evident the formation of ε phase, in addition to α and η phases, at the early stages of milling. Furthermore, these diffractograms show clearly that the intensities of α phase (111) and ε phase (0002) peaks decrease with milling time, and simultaneously the diffraction peak of τ' phase appears next to the η phase (1011)

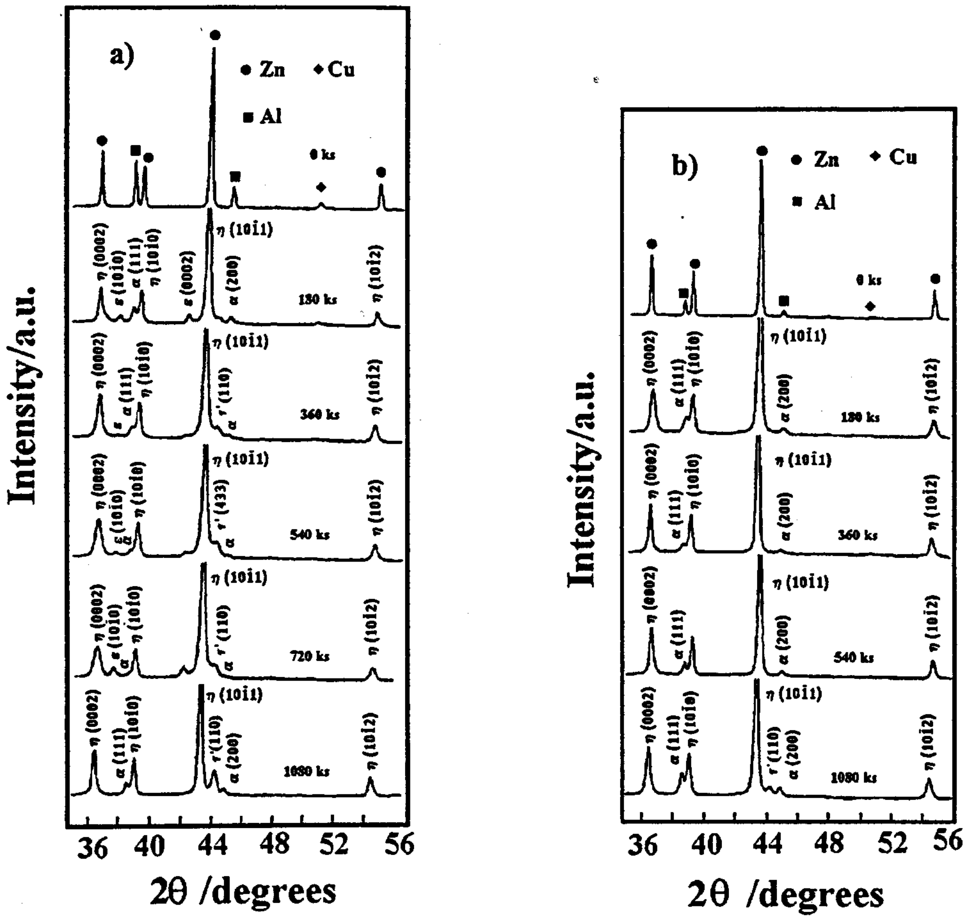

Figure 1. XRD patterns of a) the Zn-22wt.%Al-3wt.%Cu powder mixture milled for 0, 180, 360, 540 and 1080 ks and b) the Zn-20wt.%Al-10wt.%Cu powder mixture milled for 0, 180, 360, 540 and 1080 ks.

diffraction peak. This suggests that the following phase transformation $\alpha + \varepsilon \rightarrow \eta + \tau'$ took place during milling. That is, this phase transformation preceded and caused the formation of α, η and τ′ phases in both final mechanically alloyed powders, after 1080 ks of milling. The presence of these phases is in agreement with the equilibrium phases predicted for these compositions in the equilibrium Al-Cu-Zn phase diagram [4]. This type of phase transformation has been also reported to occur in the same composition alloy, obtained by melting and casting, after aging at 150 °C for 15 minutes, and also after tensile, creep tests and mechanical milling [5-8].

Figure 2 (a) shows the XRD patterns of the Zn-10wt.%Al-22wt.%Cu powder mixture milled for times up to 360 ks. These indicated that the η and ε phases are formed rapidly without the presence of the α phase during milling. These two phases remained after 1080 ks of milling.

The XRD patterns of MM Zn-22wt.%Al-2wt.%Cu alloy powder milled for different times are shown in Fig. 2 (b). It can be observed that the metastable η_{FC} phase (furnace-cooled phase) decomposed into the η_T phase (Zn-richest phase) after 3.6 ks of milling. The lattice parameter c of η phase changed from 0.486 nm to 0.492 nm after 144 ks of milling. In addition, it was also observed the presence of τ′ phase and the absence of ε phase after 144 ks of milling. This also suggests that the four phase reaction $\alpha + \varepsilon \rightarrow \eta + \tau'$ took place during the milling of this alloy.

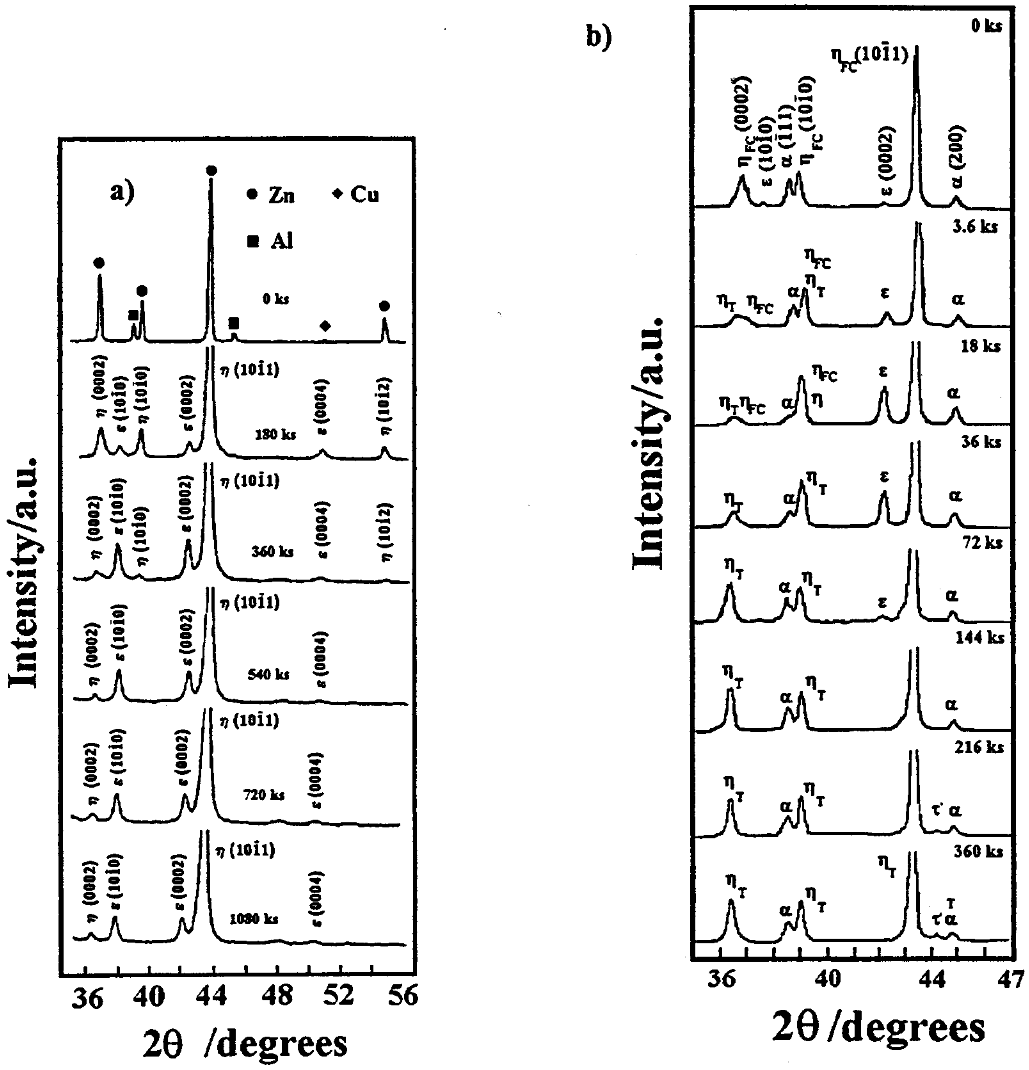

Figure 2. XRD patterns of a) the Zn-10wt.%Al-22wt.%Cu powder mixture milled for 0, 180, 360, 540, 720 and 1080 ks and b) the Zn-22wt.%Al-2wt.%Cu alloy powder milled for 0, 3.6, 18, 36, 72, 144, 216 and 360 ks.

A mixture of η, α and τ′ phases was observed after 360 ks of milling, as expected for this composition in the Al-Cu-Zn phase diagram [4].

Microstructural Characterization of Mechanically Alloyed Powders. The microstructural evolution of mechanically alloyed Zn-22wt.%Al-2wt.%Cu powders during milling is shown in Fig. 3. The first stage of milling involves powder mixture, deformation, fracture and welding of powder particles. This deformation and welding cause the formation of large flake-shaped particles containing layers of the alloy components. Further milling produces the formation of equiaxed particles, first with an oriented lamellar structure and subsequently with a random arrangement of several lamellar granules within a given particle. Finally, the microstructural refinement continues forming a fine dispersion of α phase (dark points) in the η phase matrix (bright regions). Similar results were found for the other alloy composition.

On the other hand, The microstructural evolution of MM Zn-22wt.%Al-2wt.%Cu alloy powders is shown in Fig. 4. These micrograph sequence shows that both fine and coarse lamellar structures are broken and gradually transformed into a fine dispersion of α phase in the η phase matrix during the milling process.

Figures 5 (a) and (b) shows the TEM bright field micrographs with its corresponding electron diffraction pattern of the MA and MM Zn-22wt.%Al-2wt.%Cu powders after 1080 ks of milling. Both electron diffraction patterns are composed of concentric rings corresponding to a polycrystalline alloy. The indexing of ring pattern indicates that the reflections mainly come from η phase, since the reflections of η and α phases are overlapped in both alloy compositions. A grain size from 50 to 75 nm can be observed in both TEM micrographs.

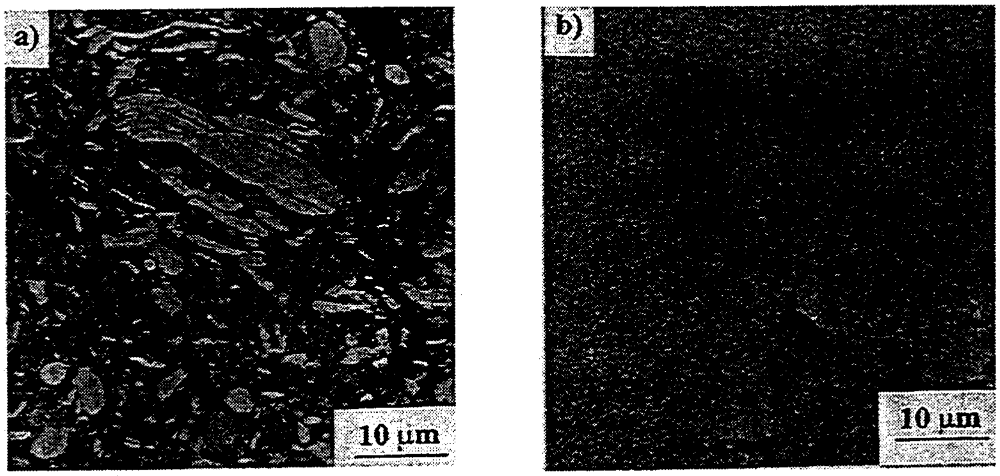

Figure 3. SEM micrographs of the Zn-22wt.%Al-2wt.%Cu powder mixture milled for a) 180 ks and b) 1080 ks.

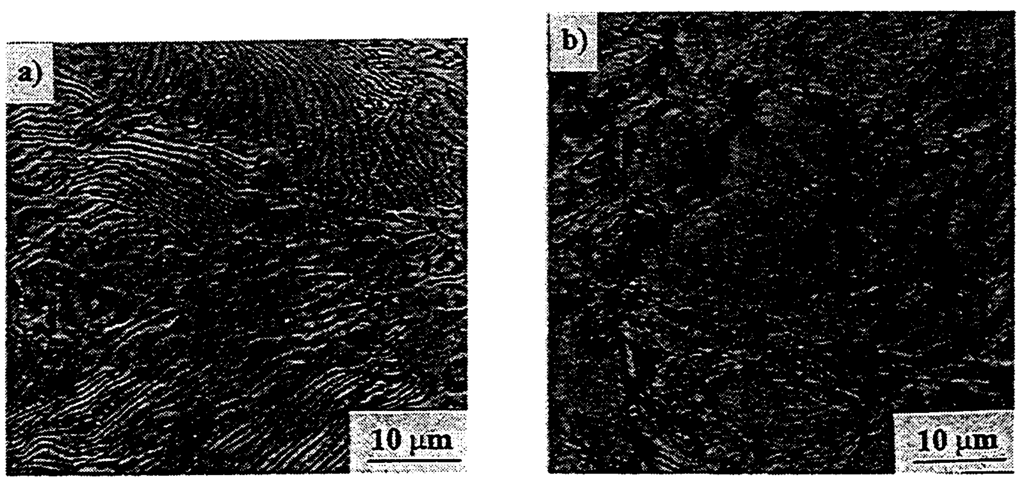

Figure 4. SEM micrographs of the MG Zn-22wt.%Al-2wt.%Cu alloy powder milled for

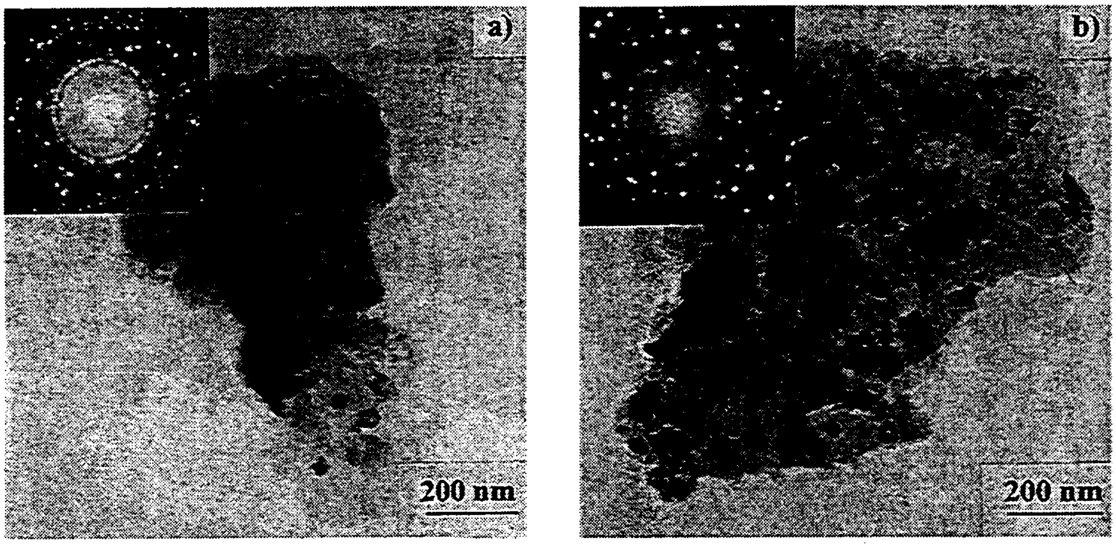

Figure 5. TEM micrographs and its corresponding electron diffraction pattern of the a) mechanically alloyed and b) mechanically milled Zn-22wt.%Al-2wt.%Cu powders after 1080 ks of milling.

Conclusions

The mechanical alloying and mechanical milling processes enabled us to produce Zn-rich Zn-Al-Cu alloys composed of nanometer size α, η and τ' phases. The formation of these phases is in agreement with that predicted for these compositions in the equilibrium Al-Cu-Zn phase diagram. It was also found that the following phase transformation $\alpha + \varepsilon \rightarrow \eta + \tau'$ occurred during both MM and MA processes.

Acknowledgments

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References

[1] B. L. Huang, and E. J. Lavernia: J. Mater. Synth. And Process. Vol. 3 (1995), pp. 1ff.
[2] Y. H. Zhu y F. E. Goodwin: J. Mater. Res. Vol. 10 (1995), pp. 1927ff.
[3] Y. H. Zhu: J. Mat. Sci. Lett. Vol. 32 (1996), pp. 1888ff.
[4] Y. H. Zhu and S. Murphy: China J. Met. Sci. Technol. Vol. 2 (1995), pp. 105ff.
[5] Y. H. Zhu, G. Torres-Villaseñor and C. Piña: J. Mater. Sci. Vol. 29 (1994), pp. 1549ff.
[6] Y. H. Zhu and J. Torres: Z. Metallkd. Vol. 88 (1997), pp. 329ff..
[7] Y. H. Zhu, E. Orozco, J. Torres: Mater. Trans. JIM. Vol. 38 (1997), pp. 521ff.
[8] Y. H. Zhu, V. M. López-Hirata and M. L. Saucedo-Muñoz: J. Mater. Process. Tech. Vol. 63 (1997), pp. 624ff.