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Mechanical Alloying of Zn-rich Zn–Al–Cu Alloys

Zn-rich Zn–Al–Cu alloys were produced by milling of elemental powders mixtures, Zn-22 wt.% Al-3 wt.% Cu and Zn-20 wt.% Al-10 wt.% Cu, for times of up to 1080 ks. The X-ray diffraction analysis showed the formation of α (aluminum-rich), η (zinc-rich) and ε ($CuZn_4$) phases at the early stage of milling. The presence of ε phase was more evident with the increase of copper content in mixture. In the case of the two alloy compositions, the following phase transformation $\alpha + \varepsilon \rightarrow \eta + \tau'$ was observed to occur during milling. A mixture of η, α and τ' phases was found in powder mixtures milled for 1080 ks, which is in agreement with phases predicted for these compositions in the equilibrium Al–Cu–Zn phase diagram. Finally, all these phases were present on a nanometer scale in both mechanically alloyed powders.

1 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]. The polycrystalline alloys, obtained by this process, have the characteristic of forming nanostructures, which are expected to attribute better physicochemical properties to these alloys [2]. However, compared to binary alloys, the processing of ternary alloys by MA has not been widely studied. 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. Additionally, we have not found any previous report on mechanical alloying in the Zn–Al–Cu system.

Therefore, the purpose of this work is to study the phase formation and microstructural evolution in Zn-rich Zn–Al–Cu alloys obtained by mechanical alloying.

2 Experimental Procedure

The following elemental powder mixtures Zn-22 wt.% Al-3 wt.% Cu and Zn-20 wt.% Al-10 wt.% Cu were prepared using pure metallic powders. These mixtures were placed into an austenitic stainless steel vial. Methanol was used as surfactant agent. Austenitic stainless steel 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 Philips diffractometer, using copper Kα radiation filtered with nickel and a scanning rate of 1 degree per minute. The mechanically alloyed 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 metallographically with 0.05 µm alumina and observed with backscattered electrons at 20 kV in a JEOL JSC-35F scanning electron microscope. The milled powders were also mounted on a carbon-coated copper-grid of 3 mm diameter and then observed at 200 kV in a JEOL 2000-FXII transmission electron microscope.

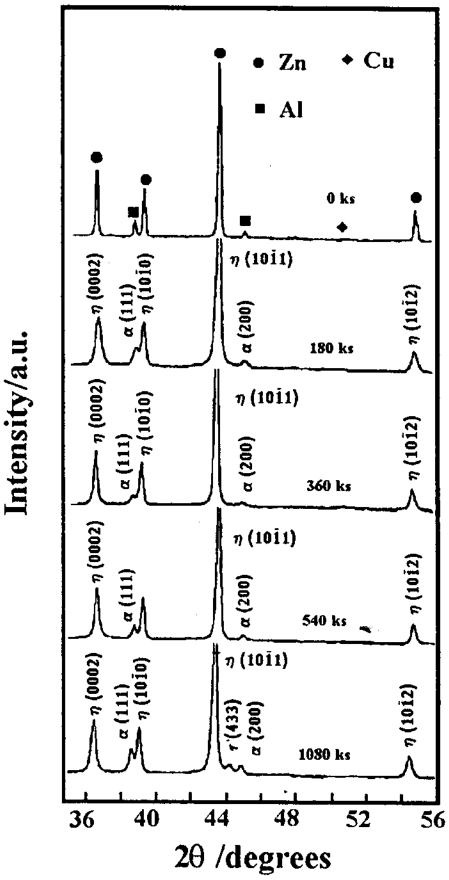


Fig. 1. XRD patterns of the Zn-22 wt.% Al-3 wt.% Cu powder mixture milled for 0, 180, 360, 540 and 1080 ks.

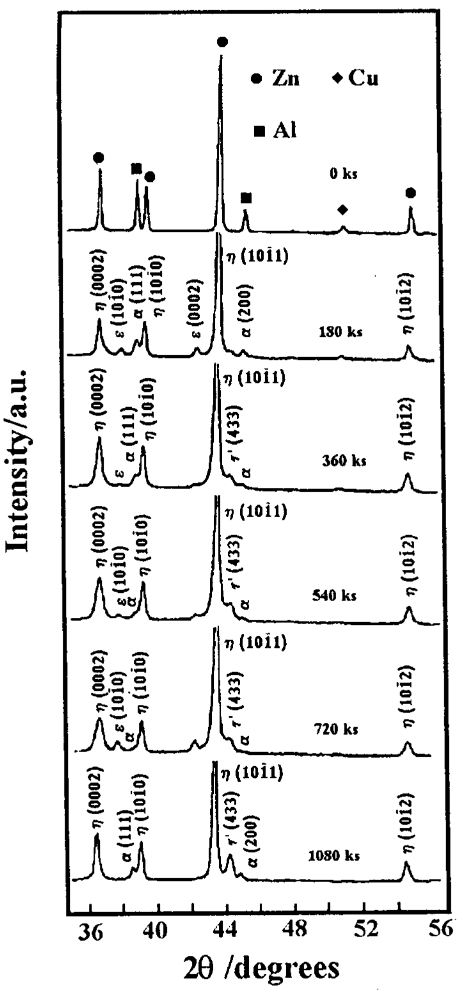


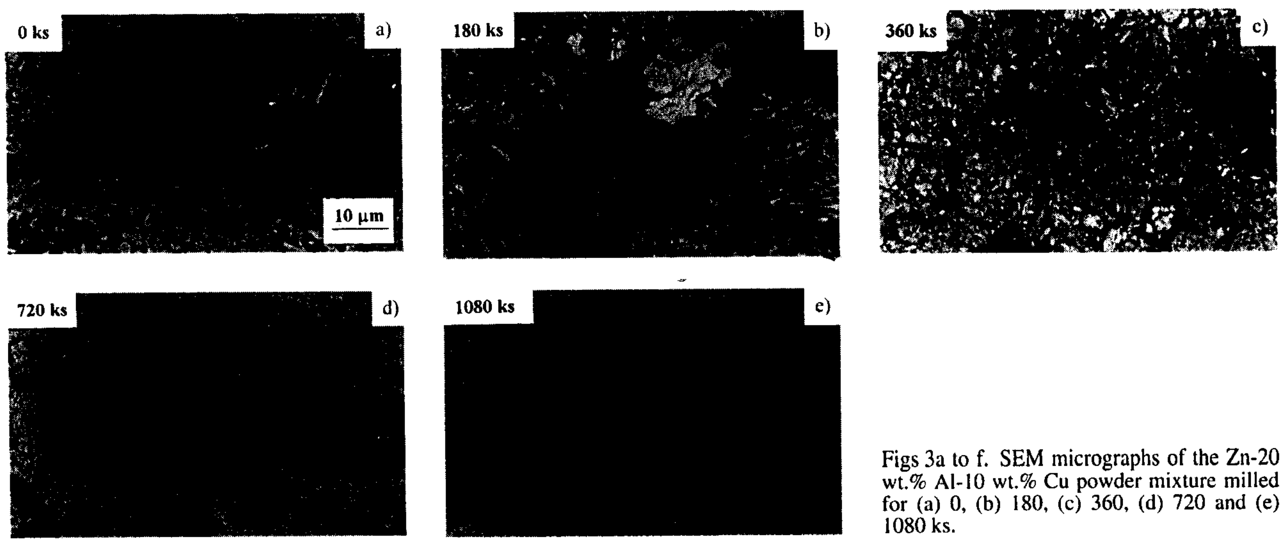
Fig. 2. XRD patterns of the Zn-20 wt.% Al-10 wt.% Cu powder mixture milled for 0, 180, 360, 540, 720 and 1080 ks.

3 Results and Discussion

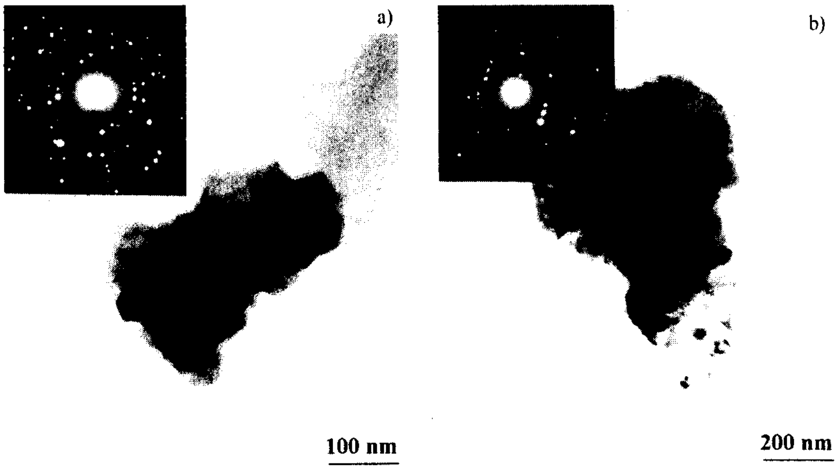
3.1 X-Ray Diffraction Analysis of Mechanically Alloyed Powders

Figure 1 corresponds to the X-ray diffraction (XRD) pattern of the Zn-22 wt.% Al-3 wt.% 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 c values for the η phase of 0.487 to 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, γ and η phases during milling. It is important to say that, according to the lattice parameter c, an increase of solubility of aluminum in zinc or vice versa has not been achieved, as reported in several immiscible binary alloys obtained by mechanical alloying [1]. An increase of the width of diffraction peaks at high 2θ angles with milling time can also be notice, 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.

To analyze the formation of τ' phase, the copper content of powder mixture was increased. The XRD patterns of Zn-20 wt.% Al-10 wt.% Cu powder mixture milled for different times are shown in Fig. 2. Here, in addition to α and η phases, the formation of ε phase is evident 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 (10$\bar{1}$1 diffraction peak). This suggests that the following phase transformation $\alpha + \varepsilon \rightarrow \eta + \tau'$ took place during milling. That is, this phase transformation preceded



Figs 3a to f. SEM micrographs of the Zn-20 wt.% Al-10 wt.% Cu powder mixture milled for (a) 0, (b) 180, (c) 360, (d) 720 and (e) 1080 ks.



Figs 4a and b. TEM micrographs and its corresponding electron diffraction pattern of a) Zn-22 wt.% Al-3 wt.% Cu and (b) Zn-20 wt.% Al-10 wt.% Cu powder mixtures milled for 1080 ks.

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 [3]. This type of phase transformation has also been reported to occur in an alloy of same composition, obtained by melting and casting, after aging at 150 °C for 15 minutes, and also after tensile creep tests and mechanical milling [4 to 7].

3.2 Microstructural Characterization of Mechanically Alloyed Powders

The microstructural evolution of mechanically alloyed Zn-20 wt.% Al-10 wt.% Cu powders during milling shown in Fig. 3, is in agreement with that described by Benjamin and Volin [8]. In other words, 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.

Figures 4a and b show the TEM bright field micrographs with its corresponding electron diffraction patterns of the Zn-22 wt.% Al-3 wt.% Cu and Zn-20 wt.% Al-10 wt.% Cu powder mixtures milled for 1080 ks. The electron diffraction pattern is composed of concentric rings corresponding to a polycrystalline alloy. The indexing of ring pattern indicates that the reflections mainly come from the 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 the TEM micrographs of both compositions. Additionally, the electron microdiffraction analysis enabled us to observe that these grains corresponded to either η phase or α phase; however, it was not possible to observe the τ' phase, which might be attributed to its low volume fraction and size.

4 Conclusions

The mechanical alloying process enabled us to produce Zn-22 wt.% Al-3 wt.% Cu and Zn-20 wt.% Al-10 wt.% Cu alloys composed of nanometer size α, η and τ' phases. These phases are in agreement with those predicted in the equilibrium Al–Cu–Zn phase diagram for these two compositions. It has also been found that the phase transformation $\alpha + \varepsilon \rightarrow \eta + \tau'$ occurred during the milling of both alloy compositions

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