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Determination of Lattice Parameters, Diffracting Crystallite Size, and Thermal Stability in Mechanically Alloyed Cu-Zn Solid Solutions

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Four copper-zinc (Cu-Zn) alloy powders are produced by mechanical alloying to investigate the effects of zinc composition on the lattice parameter, diffracting crystallite size (DCS), and thermal stability. The DCS versus either milling time or composition data indicates that the substitutional zinc solutes alter the dislocation generation, organization, and recovery processes. Lattice parameter determinations agree well with published values at small compositions, but are slightly less than the expected values for larger compositions. Annealing the powders at 823 and 1023 K for 6 h resulted in a substantial decrease of root-mean-square (rms) atomic-level strain and slight increases in the lattice parameters. In spite of the high annealing temperatures, the DCS remains less than 30 nm for all compositions. Furthermore, this high degree of thermal stability was inversely related to the concentration of zinc in the alloy.

Keywords

defracting crystallite size, mechanical alloying, nanostructured

1. Introduction

NANOSTRUCTURED MATERIALS research is being conducted in hopes of improving the properties of traditional alloys and for fabricating new materials with novel behavior. One method of producing nanostructured materials is by high-energy mechanical alloying. A mechanically alloyed material is fabricated from two or more elemental powders, either at ambient or slightly elevated temperatures (Ref 1). The alloying process fractures and welds the powder particles, resulting in atomic-level mixing, increased dislocation density, and grain size reduction to nanometer dimensions. These powders are then consolidated and heat treated at high temperatures, where diffusion processes and grain growth invariably occur. For this reason, the nanostructure grain size may not be retained in the final product. To determine the grain size stability at high temperature, this study investigates the alloying behavior and the grain size formation in a mechanically alloyed Cu-Zn solid solution.

The properties of the Cu-Zn system are well known, since brasses have been used in various applications for centuries. The similarity in the atomic size of copper (0.128 nm) and zinc (0.133 nm), combined with the slight electronegativity and valence differences, allows almost 30 wt% zinc in solution at room temperature (Ref 2). These characteristics make the Cu-Zn system ideal for studying the dissolution behavior and grain size stability of a substitutional solid solution.

The purpose of this investigation is to characterize the crystalline structure of the mechanically alloyed Cu-Zn powders and to determine what effects the zinc has on altering the as-milled powders and grain growth behavior. Four compositions of Cu-Zn powders are mechanically alloyed in a high-energy ball mill. These compositions are chosen to stay within the α-brass region (fcc) of the Cu-Zn phase diagram. These powders are analyzed in the as-alloyed and annealed conditions using x-ray diffraction techniques to determine the diffracting crystallite size (DCS) and the lattice parameter (*a*).

2. Experimental Procedure

In an argon atmosphere, copper (Atlantic Equipment Engineers, –100 mesh, 99.8%) and zinc powder (Alfa AESAR, –200 mesh, 99.9995% metals basis) are placed in a tungsten-carbide-lined milling vial, along with three 12 g tungsten-carbide (WC) balls, with a ball-to-powder mass ratio of 2. Directly prior to milling, the argon atmosphere within the vial is mixed to a 50% argon, 50% air environment using a partially evacuated transfer chamber, and the vial is sealed. This procedure is adopted to promote adherence of the powder to the ball and, hence, minimize WC contamination. The powder is mechanically alloyed using a SPEX 8000 Mixer/Mill (Sytech Corp., Houston, TX) for up to 12 h. A 0.3 g sample is taken every 2 h, and the milling atmosphere is refreshed. During milling, the vials are cooled continuously by an electric fan. The compositions of the copper and zinc powders are: Cu-0.5at.%Zn, Cu-1at.%Zn, Cu-10at.%Zn, and Cu-25at.%Zn.

X-ray spectra of the powder samples are obtained using a Philips APD 3520 x-ray diffractometer (Philips Electronics Co., Mahwah, NJ). To determine the DCS as a function of milling time, representative samples are scanned over the Cu (111) peak or the Cu (200) peak at 0.02° per step with a 10 s dwell time. For each composition, the 12 h milled samples are scanned from 40° to 150° at 0.02° per step and 10 s per step. These samples are laced with a lead standard powder to correct for peak position shifts caused by instrumental errors. A single-peak Fourier analysis technique is used to determine average diffracting crystallite size (Ref 3). The lattice parameter for each composition is determined using linear regression on data

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plotted as a versus cotθ cosθ, where θ is half the value of the maximum peak intensity (Ref 4).

Approximately 2 g of the 12 h milled sample for each composition are annealed at 873 K for 6 h in a partially evacuated Pyrex tube (Corning Glass Works, Corning, NY) supplied with a tantalum getter. Approximately 2 g of each 12 h milled sample are wrapped in tantalum foil and annealed in a Burrell high-temperature electric tube furnace at 1023 K for 6 h under flowing argon. The annealed samples are analyzed for DCS using the process described above on the Cu (111) peak.

3. Results and Discussion

3.1 *Mechanically Alloyed Samples*

The mechanical alloying process decreases the copper DCS with respect to milling time and zinc composition, as shown in Fig. 1. After only 2 h of milling, the DCSs for both compositions are below 15 nm. Since the DCS of the as-received copper powder was 37.5 nm, this indicates that the DCS is decreased by a factor of two in a short time period. Furthermore, the Cu-25at.%Zn powder has a consistently smaller DCS than the Cu-1at.%Zn for all milling times. This behavior is not completely understood. The reduction of the crystallite size and the attainment of a steady-state crystallite size are the results of the interplay and balance between several mechanisms occurring simultaneously during the milling process. For instance, in an elemental powder dislocation generation is the dominant mechanism early in the milling process, quickly followed by work hardening and recovery mechanisms (Ref 5). The addition of a substitutional solute atom, such as zinc, changes the work hardening rate and, generally, lowers the stacking fault energy. These effects can alter the dislocation formation and organization, and possibly the DCS (Ref 2). Though important, an issue that was not specifically addressed in this investigation is how quickly the zinc dissolves into the copper and what possible effects this dissolution has on the DCS.

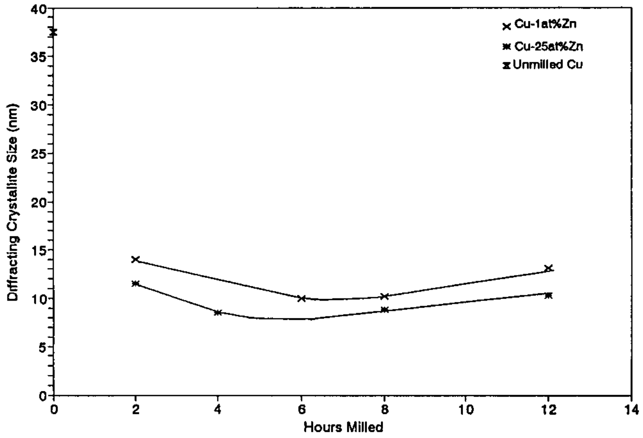

Fig. 1 Average diffracting crystallite size versus milling time for representative samples

To better compare the effects of composition on the DCS, the crystallite size versus zinc composition for the 12 h milled powder is plotted in Fig. 2. From this plot the DCS appears to be approximately constant for the 0.5%, 1.0%, and 10% powders, but decreases considerably for the 25% powder. Since increasing the zinc content increases the strength, hardness, and ductility of α-brass, the reduction of the DCS for the 25% alloy probably results from increased work hardening (Ref 6).

The x-ray diffraction patterns of the 12 h milled Cu-Zn alloys, laced with a lead standard, are shown in Fig. 3. The Cu (111), (200), and (220) peaks demonstrate slight broadening and a small shift toward a lower 2θ as the concentration of zinc in solution increases the lattice parameter. The absence of zinc peaks in the diffraction patterns for all compositions indicates that alloying between the copper and the zinc took place. These x-ray data are used to calculate the lattice parameters shown in Fig. 4, with errors of ~0.3% (Ref 4). For comparison, the known Cu-Zn lattice parameters are denoted by the dashed line (Ref 7). Good agreement is seen for the 0.5 at.% and the 1.0 at.% powders, while the higher compositions show a slight negative deviation. These results confirm that the powders are truly alloyed, and probably only very small amounts of two-phase aggregates are present.

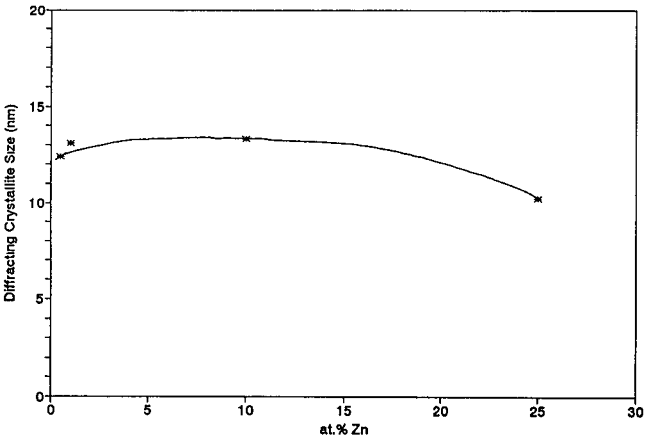

Fig. 2 Average diffracting crystallite size versus atomic percent Zn for various Cu-Zn alloys milled 12 h

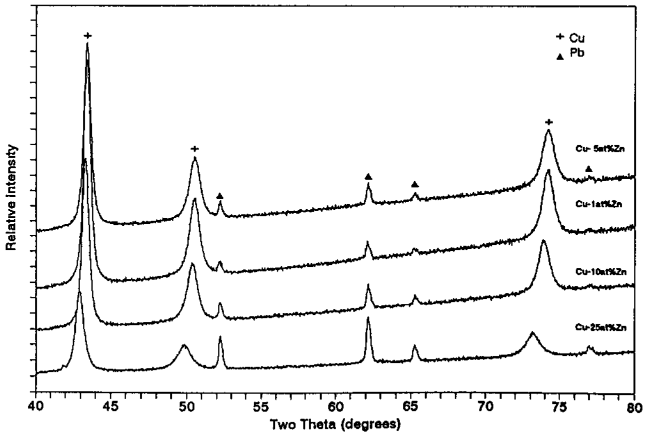

Fig. 3 X-ray patterns of various Cu-Zn alloys milled 12 h, showing Cu peaks and Pb peaks (standard)

3.2 *Annealed Samples*

Figure 5 shows the x-ray diffraction patterns for Cu-25at.%Zn, milled 12 h and annealed 6 h at 873 K. Only the copper and lead (Pb) peaks are seen in the x-ray patterns. In addition, oxide peaks are noticeably absent. These results indicate that the zinc remained in solution during and after the annealing process. Annealing the powders allows recovery, recrystallization, and grain growth to proceed. These processes manifest themselves by sharper copper peaks in the annealed powder than in the as-milled powder. Calculation of the lattice parameter for the Cu-25at.%Zn indicates an annealed parameter of 0.3673 nm compared to 0.3659 nm for the as-milled powder. The expansion of the lattice after annealing provides closer agreement with the published values. These results seem surprising since conventional thinking would indicate that the stresses are relieved upon annealing.

To investigate the amount of stored strain, the root-mean-square atomic-level strain (determined from L = 30 nm) versus composition is plotted in Fig. 6 for the as-milled and annealed specimens. The stored strain for the as-milled powder tends to increase with composition. The strains for the annealed specimens do not follow clear trends; however, for all specimens the strains decrease upon annealing, with the highest annealing temperature of 1023 K resulting in negligible strains at the higher compositions. This plot clearly indicates that recovery processes that occur during annealing strains are released upon annealing.

The effects of composition on the grain growth behavior of the annealed powders are seen in Fig. 7. In all cases, the DCS increases as the composition increases, with the largest increases accompanying the higher annealing temperature. Though the 0.5 at.% alloy data have large variations, the other alloys show that the stability of the DCS is inversely related to the composition. These results clearly indicate that the grain growth of Cu-Zn solid solutions is thermally stable at high temperatures and during relatively long annealing times. The reasons for the observed thermal stability are not understood at this time, and further work will be required. However, many two-phase nanocrystalline alloys and immiscible alloys have shown similar thermal stability (Ref 8, 9).

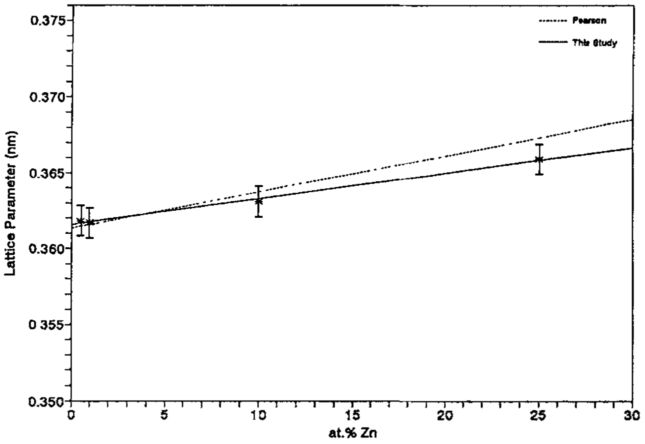

Fig. 4 Lattice parameter versus atomic percent Zn for Cu-Zn alloys

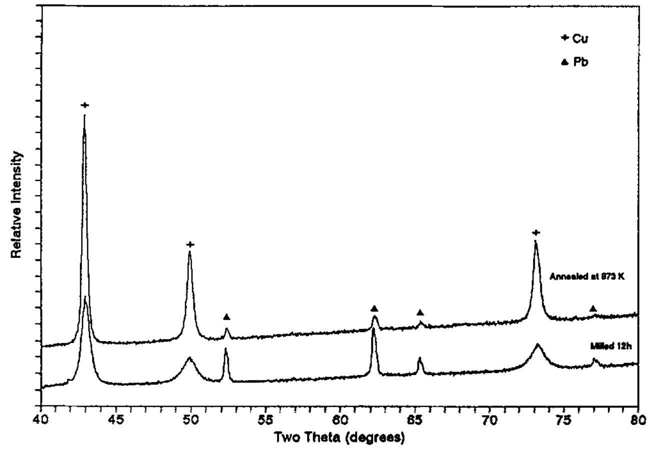

Fig. 5 X-ray patterns of milled and annealed Cu-25at.%Zn showing Cu peaks and Pb peaks (standard)

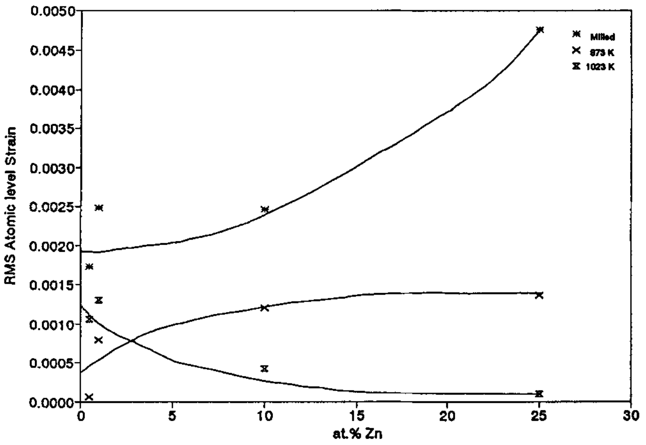

Fig. 6 Root-mean-square atomic level strain versus atomic percent Zn for Cu-Zn alloys milled 12 h and annealed 6 h at 873 K and 1023 K

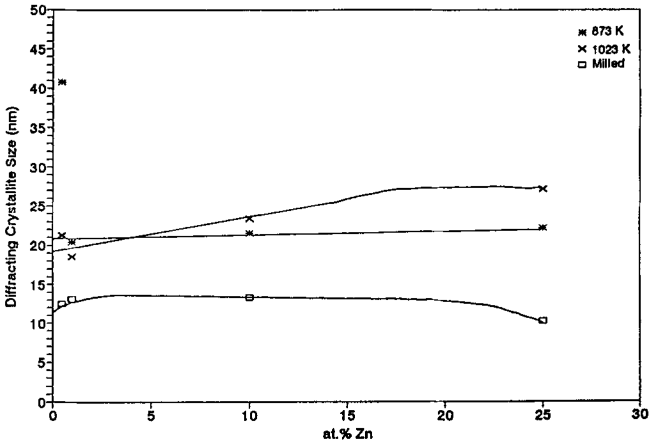

Fig. 7 Average diffracting crystallite size versus atomic percent Zn for Cu-Zn alloys milled 12 h and annealed 6 h at 873 K and 1023 K

4. Conclusions

The effects of zinc composition on the lattice parameter, diffracting crystallite size (DCS), and thermal stability for mechanically alloyed Cu-Zn powders are investigated. X-ray diffraction analysis shows that milling for 12 h results in complete alloying. The DCS versus either milling time or composition data indicates that the substitutional zinc solutes alter the dislocation generation, organization, and recovery processes. Lattice parameter determinations agree well with published values at small compositions but are slightly less than the expected values for the larger compositions. This is an unexpected result that is not completely understood at this time. Annealing the powders results in a substantial decrease of the mean atomic-level strain and slight increases in the lattice parameters. Annealing at 823 and 1023 K for 6 h resulted in DCSs less than 30 nm for all compositions. Furthermore, this high degree of thermal stability is inversely related to the concentration of zinc in the alloy.

Acknowledgments

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