Materials Research, Vol. 8, No. 2, 169-172, 2005

Evaluation of Mechanical Alloying to obtain Cu-Al-Nb Shape Memory Alloy

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Received: November 23, 2003; Revised: December 28, 2004

The technical viability of preparing a Cu-Al-Nb shape memory alloy by high energy ball milling in a planetary mill has been evaluated. The alloy Cu-13Al-2Nb (wt. (%)) was prepared by mixing pure elemental powders. A ball-to-powder weight ratio of 6:1 and rotation rate of 150 rpm in argon atmosphere were the main processing parameters. The milling time ranged from 1 to 65 hours. Changes in microstructure as a function of milling time were investigated, using X-ray diffraction analysis and scanning electron microscopy. To investigate the viability of producing sintered parts from milled powders, the conventional powder metallurgy route was used. The milled powders were compacted in a cylindrical die at 900 MPa. Sintering was carried out in argon atmosphere at 850 °C for 6 hours. This study has shown that high energy ball milling, combined with pressing and sintering, can be used to promote the formation of a copper-aluminum solid solution and achieve final sintered densities of 91% of the theoretical density.

Keywords: *powder metallurgy, mechanical alloying, sintering*

1. Introduction

Shape memory alloys (SMA) are now conventional functional materials with intrinsic characteristics that differentiate them from other materials. SMA return to their original form when plastically deformed at certain temperatures above room temperature. The main characteristic of these materials with shape memory effects is diffusionless phase transformation (martensitic transformations).

In recent years, Cu-based SMAs have been widely developed because of their relatively low cost and simpler manufacturing process, compared to Ni-Ti SMA. Among Cu-based SMAs, the CuAlNb system has better thermal stability[1]. Hence this system was selected for study. In conventional casting, alloy grain size is difficult to control. Coarse grains deteriorate the mechanical properties of the alloys. It has been reported that mechanical alloying (MA) and powder metallurgical techniques (P/M) can be used to prepare Cu-based SMAs[2,3]. MA can reduce oxidation because a new phase is formed, and produces a pre-alloyed powder that shortens the sintering time. In this study, high energy planetary ball milling was used to convert the Cu-Al-Nb elemental powder mixture into pre-alloyed powders. The purpose of this investigation is to evaluate mechanical alloying as a process to obtain Cu-Al-Nb alloys with shape memory effects, with or without the addition of lubricants.

2. Experimental Procedures

2.1. Preparations of pre-alloyed powders

A planetary ball mill Fritsh Pulverisette® with four stainless steel vials was used in the MA process. Each vial contained hardened steel balls with diameters of 20 mm, 10 mm, and 5 mm. The ball-to-powder weight ratio (BRP) was 6:1. The average particle size and purity of the elemental powders and the composition of the mixture are shown in Table 1.

The vials sealed with O-rings were evacuated inside a glove box and argon gas injected to avoid oxidation of the powders during the milling stage.

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2.2. Cold compaction and sintering

Compaction was carried out in a 40-ton hand-operated hydraulic press and a single-action die, 4-5 mm high and with bore diameter of 9.6 mm. The die wall was lubricated with zinc stearate. The pre-alloyed powders were compacted at a pressure of (900 MPa), to form disc-shaped green compacts. The compacts were sintered in a tube furnace at 950 °C for 6 hours in protective high purity (99.999%) argon atmosphere, and furnace cooled. The sintered compacts were solution-treated at 900 °C for one hour followed by quenching in water to room temperature.

2.3. Techniques used to characterize the powders and compacts

a) Density measurement: ASTM designation 311-93;
b) X-ray diffraction analysis: Siemens D5000 diffractomete using CuKα radiation;
c) Optical microscopy: specimens were etched with 20% Nital solution;
d) Scanning electron microscopy (SEM);
e) Differential scanning calorimetry (DSC).

3. Results and Discussion

3.1. Compaction pressure

The compaction pressure was determined from the green density versus compaction pressure curve. The pressure selected was 950 MPa and it was kept constant.

3.2. X-ray diffraction analysis

3.2.1. Samples milled without a lubricant

Figure 1 shows changes in the structure of the Cu-Al-Nb powder mixture without a lubricant, as a function of milling time.

Figure 1 shows the diffractograms of the Cu-Al-Nb alloy powder

milled for different times. After 3 hours of milling, the positions of the 2 θ peaks of Cu-Al are the same as that of the elemental powder, indicating that no significant reaction had occurred during milling. However after 8 hours of milling, the aluminum peak height decreased indicating that a Cu (Al) solid solution had started forming. The copper peak is displaced slightly to the right, indicating an increase in the cell parameter of Cu, due to dissolution of Al. Upon increasing the milling time, the Al peaks decrease. It can be seen that after 10 hours of milling there is only one small aluminum peak. This indicates that at this stage of milling the formation of Cu (Al) solid solution is almost complete. It is also interesting to note that other small peaks emerge. These peaks marked with X coincide with the peaks of orthorhombic martensite 2H, suggesting that these could be of a martensitic structure induced by deformation during the milling process[4].

3.2.2. Samples milled with a lubricant

Figure 2 shows the diffractograms of the mixture Cu-13Al-2Nb with 1% (by weight) of the lubricant zinc stearate. In this case, formation of a solid solution is sluggish, compared to the alloy mixture milled without a lubricant. Even after 65 hours of milling, large Al peaks can be seen. The lubricant forms a protective film on the powder surface and hinders diffusion between Al and Cu.

3.2.3. Sintered sample

The diffraction pattern in Figure 3 shows clearly the formation of an alloy between Cu and Al, resulting in a mixture of a solid solution Cu (Al) and the γ_2 phase.

3.2.4. Quenched sample

Figure 4 shows the X-ray diffractogram of Cu-13Al-2Nb quenched in iced water from 850 °C. An interesting feature of this diffractogram are the peaks lying between 2θ 30 to 50, representing martensite structures 18 R. The profile of this diffractogram is quite similar to that of molten Cu-Al-Ni SMA reported by Zhang et al.[5]

Table 1. Average particle size, purity of the elemental powders and composition of the mixture.

	Cu	Al	Nb
Average particle size (μm)	75	75	75/44
Purity (%)	99	99.9	99.9
Mixture composition (wt. (%))	85.0	13.0	2.0

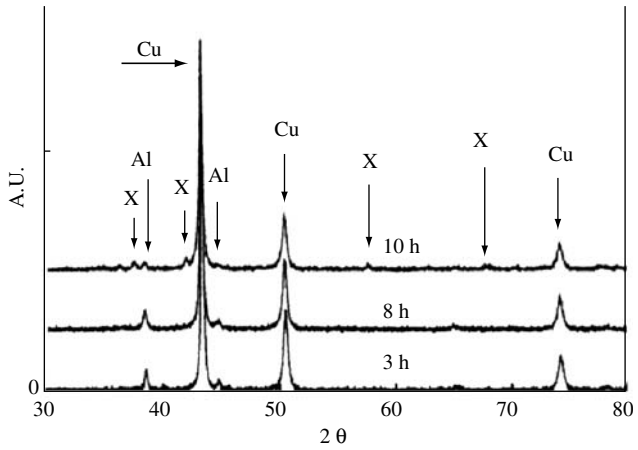

Figure 1. X-ray diffractograms of powder milled for different times at 150 rpm without a lubricant.

3.3. Differential scanning calorimetric analysis

Figure 5 presents the thermogram of an annealed sample and shows clearly the two exothermic reactions in the temperature range 275 to 450 °C.

The first peak has been attributed to relaxation in the microstructure, therefore the second peak is considered to be due to γ phase formation[4]. There is an overlap of two heat outputs, causing inaccuracy in the determination of the temperature at which γ phase formation begins. However, this was estimated by extrapolating the curve, and found to be 350 °C. The average density of the samples without a lubricant and compacted at 950 MPa was found to be 6.12 g/cm^3, which is 91% of the theoretical density of the material (6.72 g/cm^3)

3.4. Particle morphology

The particles were examined by scanning electron microscopy. Figures 6 and 7 show particles milled for 5 and 10 hours without a lubricant. The particles are rounded and the average size is between 10-25 μm.

Agglomeration of the particles can also be seen in Figure 6, indicating welding during the milling stage. Particles milled with a lubricant reveal irregular shapes and differences as a function of milling time, as shown in Figures 8 and 9. The average size of the particles depends

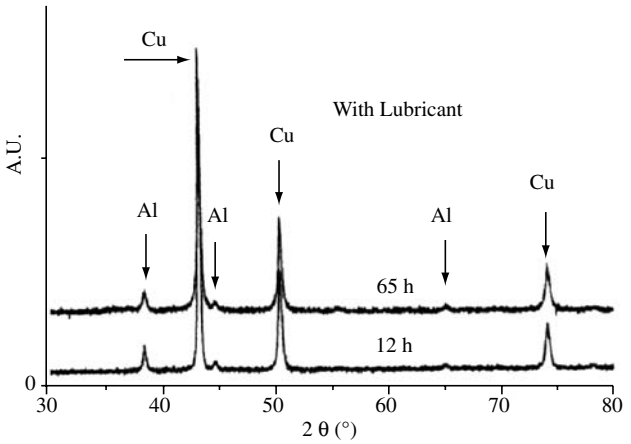

Figure 2. X-ray diffractograms of Cu-13Al-2Nb alloy with 1% zinc stearate milled at 150 rpm for different times.

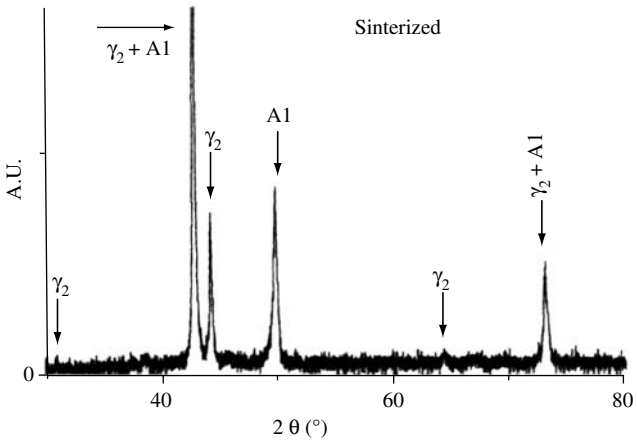

Figure 3. X-ray diffractogram of sintered Cu-13Al-2Nb alloy.

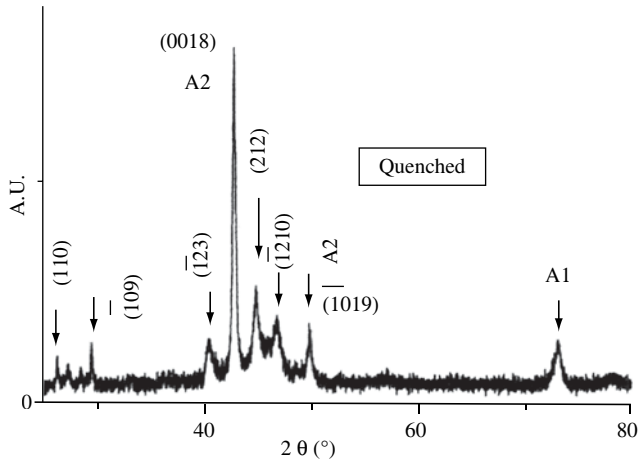

Figure 4. X-ray diffractogram of Cu-13Al-2Nb alloy quenched in ice water from 850 °C.

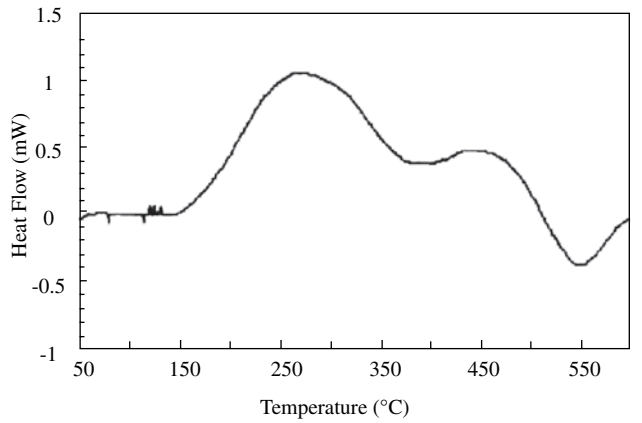

Figure 5. DSC thermogram of an annealed sample milled without a lubricant.

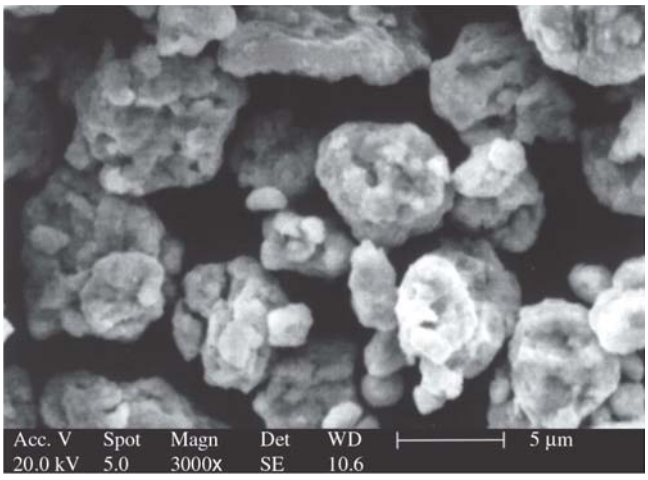

Figure 6. Scanning electron micrograph of Cu-13Al-2Nb milled for 5 hours without a lubricant.

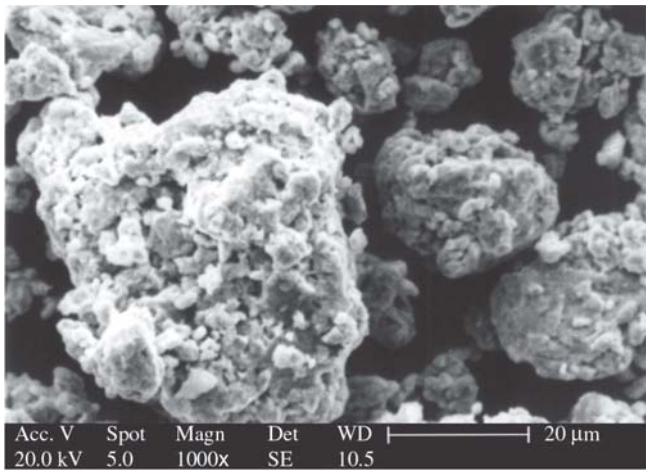

Figure 7. Scanning electron micrograph of Cu-13Al-2Nb milled for 12 hours without a lubricant.

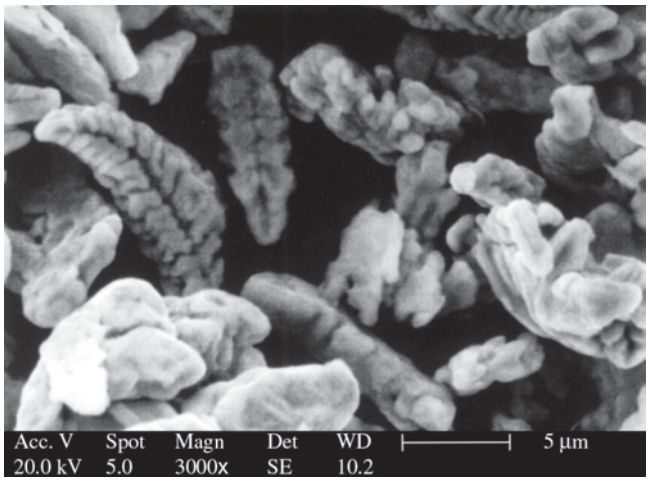

Figure 8. Scanning electron micrograph of Cu-13Al-2Nb milled for 12 hours with a lubricant.

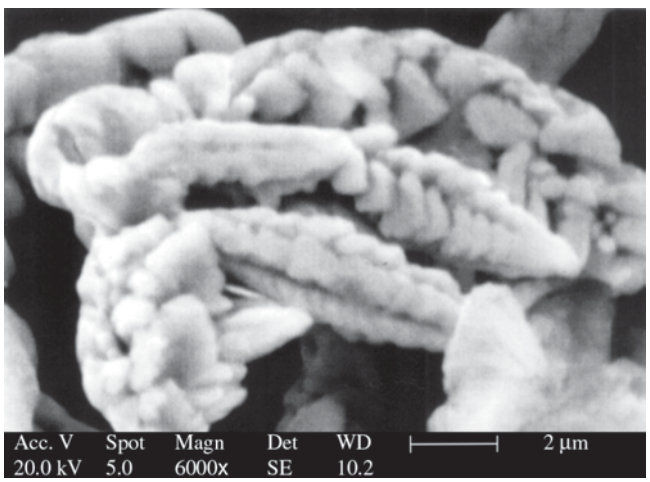

Figure 9. Scanning electron micrograph of Cu-13Al-2Nb milled for 12 hours with a lubricant.

on the extent of welding and fragmentation. In the case of milling with a lubricant, the decrease in particle size is less marked.

4. Conclusions

- Sintering of the milled powder can only be achieved after the dissolution of aluminum in copper. Otherwise the high stability of aluminum oxide prevents diffusion;
- A solid solution of aluminum in copper can be obtained by high energy milling in a planetary ball mill;
- The lubricant has a marked influence on the mechanisms of welding and fragmentation, interfering thereby in the kinetics of alloy formation;
- Samples without a lubricant attained densities of 6.12 g/cm^3, representing 91% of the theoretical density;
- The martensitic 18R structure was obtained after heat treatment. This structure is essential in shape memory alloys;

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