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Synthesis and characterization of nano structured Cu–Al–Mn shape memory alloy by mechanical alloying

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ABSTRACT

In this study, Cu-based shape memory alloy (Cu-12.5%Al-5%Mn in %wt) was processed by mechanical alloying in different milling conditions (2.5, 5, 10, 15 and 25 h). Prepared powders were characterized by means of X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). XRD results showed that increasing milling time leads to a reduction in crystallite size and an increase in lattice parameters. After 15 h of milling, the minimum crystallite size was found to be around 7 nm, and did not change upon further processing. SEM and TEM results showed that morphology of pre-alloyed powder changed with milling time from lamella to globular and the mean size of pre-alloyed powders was around 15 nm after 15 h of milling. EDX analysis results indicated a homogeneous distribution of Mn and Al elements within the Cu matrix.

1. Introduction

Since the introduction of mechanical alloying (MA) technique by Benjamin [1], it has been widely used to produce dispersion strengthened alloys [2,3]. In this technique, high energy collisions of the balls and also, the balls and the vial, lead to repeated cold welding and fracturing of powders, and eventually formation of alloyed powder.

Structural materials with a combination of high strength and high damping capacity are vastly needed in engineering applications. It is often difficult to satisfy these two requirements at the same time. But this may be achieved by the alloys exhibiting martensitic phase transformation (MT) [4,5]. Thus, materials such as shape memory alloys (SMA) seem to be very practical for this purpose. SMAs and their MT behavior have been studied for many years [6–8] and it is well known that Ni–Ti, Cu-based and Fe-based SMAs exhibit shape memory effect (SME) associated with MT. Cu-based SMAs have been developed in 1960s [9] and have simpler production procedures and lower production costs than Ni–Ti-based SMAs and they show better SME, superelasticity (SE) and two-way memory effect (TWME) than Fe-based alloys [10–12]. However, Cu-based polycrystalline SMAs are brittle due to their high elastic anisotropy ($A = 13$) and high degree of order in the β-parent phase, which restrict use of these SMAs to practical fields [13–15].

Cu–Zn–Al and Cu–Al–Ni have been extensively studied over the years [16,17]. It is been shown that among Cu-based SMAs, Cu–Al–Ni alloys have better thermal stability and may be used at higher temperature [18] while Cu–Zn–Al alloys exhibit shape memory within a certain range of composition [17]. However, practical applications of Cu–Al–Ni and Cu–Zn–Al alloys are limited to those requiring very small shape changes, due to their poor workability and susceptibility to brittle intergranular cracking. Kainuma et al. [19,20] have found that Cu–Al–Mn SMAs with a low Al content show excellent ductility because of the low degree of order of $L2_1$ parent phase. Shape memory effects of ductile Cu–Al–Mn based SMAs are achieved by MT from $\beta_1(L2_1)$ to monoclinic $\beta'_1(6M)$. For these interesting properties, Cu–Al–Mn alloy system is selected in this study.

Conventional production methods such as casting do not allow modifying chemical composition and grain size of Cu-based SMAs. Even slight variations in Al and Mn content of the alloy, strongly shifts transformation temperatures [21–23]. Also, coarse grains do not favor high mechanical properties [21]. To compensate for these drawbacks, new fabrication methods are required that allow full control over transformation temperatures and SME and PE properties.

In this study, mechanical alloying process with different milling time was employed to produce Cu-12.5%Al-5%Mn alloy from Cu, Al and Mn elemental powders mixture and then the

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Table 1
Specification of elemental powders and mixture.

	Cu powder	Al powder	Mn powder
Size (μm)	<63	<200	<63
Purity (%)	99.7	99.9	99.5
Composition of mixture (%wt)	82.5	12.5	5

prepared powders were studied to find the effect of milling time on microstructure.

2. Experimental procedures

For the MA process, a planetary mill (Fritsch P6) with hardened steel balls (10 mm in diameter) was utilized. The ball to powder weight ratio (BPR) used was 15:1. The specification of elemental powders and the initial mixture are given in Table 1. Process was carried out in argon atmosphere to avoid oxidation of the powders. The mixture was then milled for 2.5, 5, 10, 15 and 25 h at a speed of 300 rpm.

Part of milled powders was taken after certain milling time (at 2.5, 5, 10, 15 and 25 h) from the container and investigated using X-ray diffraction (XRD) with CuK_α radiation by a PHILIPS-PW1800 diffractometer.

Microstructural evaluation and morphology of the powders were studied by Hitachi S-4160 scanning electron microscopy (SEM). The EDX analysis was done for investigating the effects of milling time on diffusion and elemental distribution in the matrix. Transmission electron microscopy (TEM) was used for observation of produced powders structure in higher magnifications.

3. Result and discussion

3.1. XRD analysis

XRD patterns of produced powder with different milling times are shown in Fig. 1. The pattern of 0 h MAed powders is taken as the reference where the diffraction peaks of initial elemental powders of Cu, Al and Mn appear.

The intensities of all diffraction peaks decrease with milling time while the width of Cu peaks increase and the position of

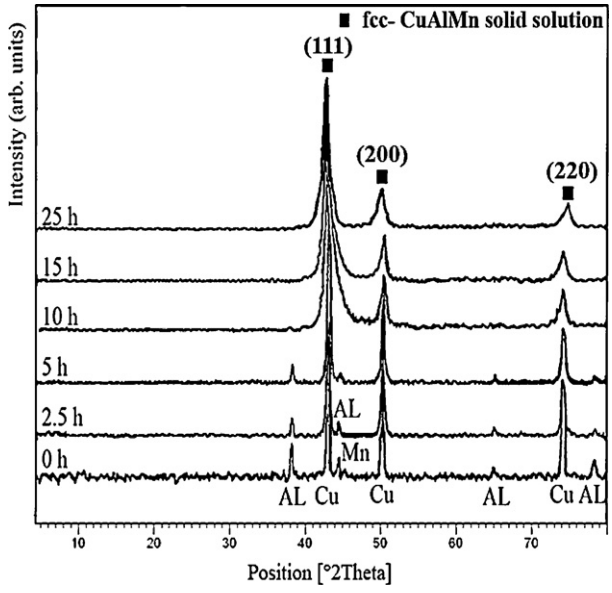

Fig. 1. X-ray diffraction patterns of powder milled after different time at 300 rpm.

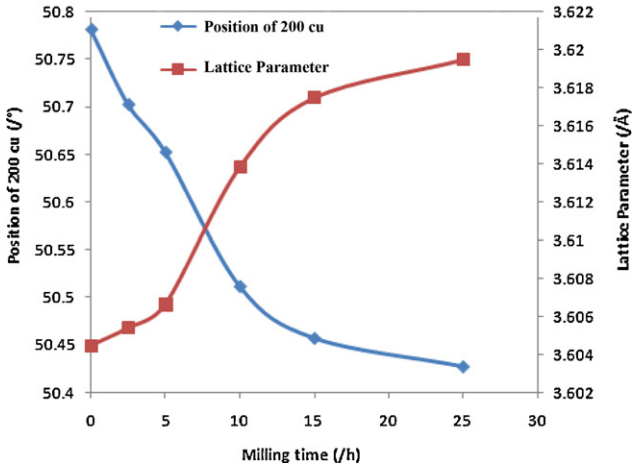

Fig. 2. Changes of peak positions and lattice parameters of Cu matrix as a function of milling time.

Cu diffraction peaks move towards lower angles (see Fig. 2), indicating the diffusion of Al and Mn atoms into the Cu matrix and an increase in lattice parameters of Cu matrix with milling time. Also, reduction in intensities of Al and Mn peaks becomes more and these peaks disappear finally after 15 h milling time.

After 15 h of MA, only the diffraction peaks of a single phase with FCC structure appear (see Fig. 1). The X-ray diffraction results lead to the conclusion that a single phase solid solution with a lattice parameter close to Cu lattice parameter is formed after 15 h MA of the elemental powder mixtures at 300 rpm.

Crystallite size (d) and micro strain (S) can be calculated from Williamson–Hall equation (as mentioned in Eq. (1)) for each produced powder.

$$\sqrt{\beta_i^2 - \beta_0^2}\cos\ \theta = \frac{0.89\lambda}{d} + S\cdot\sin\ \theta \quad (1)$$

In this equation, β_i and β_0 are estimated from full-width at half-maximum (FWHM) values of the diffraction peaks of XRD patterns of milled and unmilled samples, respectively. Since the diffraction angle (2θ) and CuK_α wave length (λ) are known, using Eq. (1), for each peak a point is made on a diagram with $\sqrt{\beta_i^2 - \beta_0^2}\cos\ \theta$ and $\sin\ \theta$ axis. Then a linear function is fitted to the diagram, is which case, Y-intercept would be $0.89\lambda/d$ and the slope of the function would be S, and d and S are thus measured, respectively.

Results from Eq. (1) show that crystallite size decreases with milling time but reduction in crystallite size is not continuous and after 15 h milling time, it becomes constant and further milling only leads to an increase in micro strain. It is shown in Fig. 3 that crystallite size decreases with milling time while micro strain increases, and the final crystallite size of CuAlMn solid solution is 7 nm after 15 h milling time.

3.2. SEM observations and EDX analysis

Fig. 4 shows the SEM images of produced powders. This figure shows that distribution of powders size and powders morphology become uniform with milling time.

Fig. 5 shows the microstructural evolution of MAed powders in higher magnification. Fig. 5(a) shows that microstructure of MAed powder is lamellar and welding has occurred between these lamellae due to ball impacts, but the spaces between these lamellae are high. The layers are thick and after 2.5 h MA, their thickness is not homogeneous. Increasing milling time to 5 and 10 h, the laminated structure becomes discontinuous and the thickness of the