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ORIGINAL PAPER

Investigation of Magnetic Properties of Phase Transformations in Copper-Based Alloys

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Abstract In this study, the magnetic properties of both $Cu_{85.41}Al_{9.97}Mn_{4.62}$ and $Cu_{82.41}Mn_{13.81}Al_{3.78}$ (wt%) shape memory alloys were studied. The analysis of the magnetization as a function of applied field and temperature was conducted between −10 to 10 T magnetic field ranges at constant temperature. Two alloys were examined using ac magnetic susceptibility measurements. The magnetic saturation values at room temperature were found to be approximately 1 and 70 emu/g for $Cu_{85.41}Al_{9.97}Mn_{4.62}$ (wt%) and $Cu_{82.41}Mn_{13.81}Al_{3.78}$ (wt%) alloys, respectively. The magnetic saturation and the coercivity values for the CuAlMn alloy are found smaller than those for the CuMnAl alloy. Moreover, from the magnetization curves, the typical ferromagnetic behavior were observed for both alloys. Details of the morphological properties and chemical composition have been examined by scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX), respectively.

Keywords Ferromagnetic shape memory alloys · Saturation magnetization · Temperature · Martensite · Austenite

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1 Introduction

The magnetic properties of ferromagnetic shape memory alloys (FSMAs) have been the subject of several works until today [1–5]. The ferromagnetic shape memory alloys have been developed by the Heusler alloy system [6–8]. Heusler reported that the addition of *sp* elements turns the Cu–Mn alloy into a ferromagnetic material although the alloy contains ferromagnetic elements [9]. Most of the FSMAs are Heusler alloys and they exhibit shape memory and magnetic behavior. The magnetic shape memory effect was studied by Ullakko et al. in 1996 for the first time [10]. Much work has already done on these alloys, partly because of great technical interest in the mechanical, electrical, and magnetic properties of this alloy system. Magnetic properties of CuAlMn and CuMnAl were experimented, and differences in heat treatment seem to affect the magnetic property [11]. Therefore, it is interesting to survey the phase transformations in these alloys. Crystal structure, composition, and heat treatment were found to be important parameters for determining magnetic properties. Some parameters can be changed with temperature, external stress, and the applied magnetic field. Therefore, it has attracted much attention as a fast responsive actuator, transducer, and functional material. This study adresseses the behavior of CuAlMn and CuMnAl ferromagnetic shape memory alloys, which was prepared in an arc furnace under argon atmosphere using high-purity Cu, Al, and Mn (99.9 %) powders. Worked alloys have amazing magnetic properties. CuAlMn and CuMnAl alloys are ferromagnetic even though its atomic constituents are nonferromagnetic. Cu-based alloys have disordered β phase at high temperatures. Upon cooling, ordering transition takes place depending on alloy composition and cooling rate. These ordered structures are with B2-, DO_3-, or $L2_1$-type superlattices, and these ordered structures then transform into martensite phase with further cooling [12, 13]. During quenching from the phase region, these alloys undergo a sequence of ordering reactions: β(A2)→ β_2(B2)→ β_1(L2_1). Three types of martensites, $\alpha\prime$(3R), $\beta\prime_1$(18R), and $\gamma\prime_1$(2H), formed depending on the amount of aluminum and manganese present in the alloys [14]. The aim of the present study is to investigate the magnetic properties of the phase structures for $Cu_{85.41}Al_{9.97}Mn_{4.62}$ and $Cu_{82.41}Mn_{13.81}Al_{3.78}$ alloys.

2 Experimental Procedure

Experimental alloys used for this study have the compositions $Cu_{85.41}Al_{9.97}Mn_{4.62}$ and $Cu_{82.41}Mn_{13.81}Al_{3.78}$ (in wt%). Bulk samples used in the SEM observations of the alloy and in various states were observed following standard metallographic procedures. The polished surface was etched at room temperature using a solution composed of 2.5 g $FeCl_3 \cdot 6H_2O$ and 48 ml methanol in 10 ml HCl. Polished and etched SEM observations were made using a JEOL 5600 scanning electron microscope, operated at 20 kV. Magnetic properties of the samples were measured by using a vibrating sample magnetometer (VSM) at room temperature. The ac magnetic susceptibility was performed as a function of temperature in the range from 0 to 300 K.

3 Results and Discussion

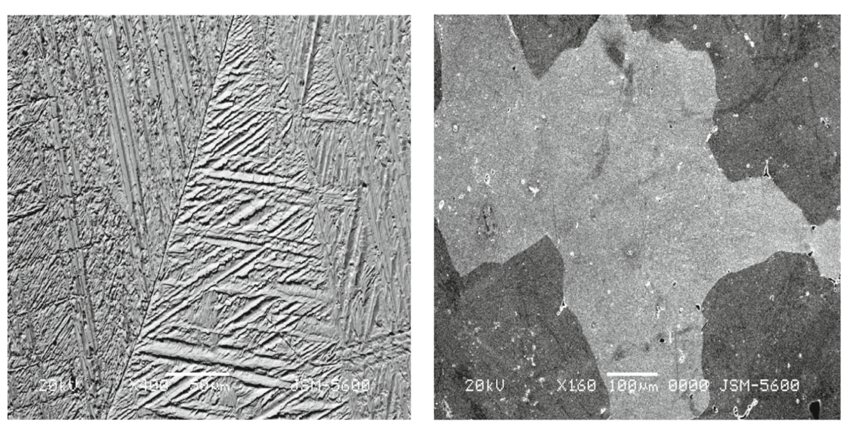
3.1 Structural Properties

Figure 1a and b shows the scanning electron micrographs of alloys. Compared to Fig. 1a and b exhibits the martensite phase. Martensite structures have different orientations in different grains [15, 16]. In CuAlMn alloy, two different martensitic phases are formed. These martensites are $\beta\prime_1$(18R) and $\gamma\prime_1$(2H). The $\gamma\prime_1$ formed as coarse variants/plates, while the $\beta\prime_1$ formed as zigzag martensitic plates [17, 18].

Austenite phase was obtained in the CuMnAl as seen in Fig. 1b. The color of each grain was observed in different shades. A grain is a portion of the material within which the arrangements of the atoms are identical; however, the orientation of the atom arrangement, or crystal structure, is different for each adjoining grain [19]. The result of this SEM is shown in which the phases display different results for CuAlMn and CuMnAl alloys. This result can be explained in Cu-based shape memory alloys, in which a change occurs with the effect of different thermal treatments in the phase transformations of the investigated alloys. Moreover, phase transformations are very sensible to the chemical composition and thermal treatments. These effects may cause important changes on crystallographic and structural properties or the other transformation parameters of these alloys [19, 20].

3.2 Magnetic Properties

Figure 2a and b shows the curves of magnetic moment change with the applied field obtained at 300 K for the CuAlMn and CuMnAl alloys. From the curves, two important values are provided: one of them is the saturation magnetization and the other is the coercivity value of the alloys. The magnetic saturation values of CuAlMn alloy are measured at 10 kOe and 1 emu/g. In the CuMnAl alloy, the applied magnetic field is shifted to 15 kOe and the magnetic moment to 70 emu/g. This was a very high value in comparison to those obtained for other CuMnAl alloys. And also, this result with those obtained in previously conducted works indicated that the coercivity value was very high [21, 22]. The magnetic saturation and the coercivity values in the martensite state (CuAlMn alloy) are found smaller than those in the austenite state (CuMnAl alloy). This result strictly originates from the different



(a) (b)

Fig. 1 SEM images of the **a** CuAlMn and **b** CuMnAl alloys crystal structures of these alloys. This study also shows the difference between the magnetization in the martensitic state and the austenitic state. The magnetization curve in the CuAlMn alloy at 300 K is slightly convex, while that in the CuMnAl alloy at 300 K shows a typical ferromagnetic behavior. Figure 2a and b excludes the simple superparamagnetic behavior of the ferromagnetic Mn pairs, which indicates the existence of magnetic interactions among them. The Mn–Mn pairs are responsible for the ferromagnetic character of these alloys. This is promoted by neutron diffraction observations that only the Mn atoms possess a magnetic moment. The results are in agreement with the literature that the Mn–Mn interactions can be ferromagnetic depending on the relative orientation of Mn atoms [1, 3, 23–25]. This situation means that the magnetic properties of worked alloys are highly sensible to the distance between Mn–Mn pairs [1]. Cu-based shape memory alloys have disordered β phase at high temperatures. Upon cooling, either 18R or 2H martensite takes place by stress and cooling. Copper-based ternary alloys have the DO_3 (or $L2_1$)-type superlattice prior to the transformation, and stacking sequence is AB′CB′CA′CA′BA′BC′BC′AC′AB′ (18R) in martensitic case and AB′AB′AB′ (2H) in martensite-state planes [26]. Figure 3a and b gives the magnetization changes as a function of temperature for alloys. The magnetic response of a material is often probed as a function of temperature (T) under a constant applied magnetic field (H). Then, a 0.499 kOe magnetic field was applied and kept constant. The magnetization is decreased with increasing temperature in the martensitic CuAlMn alloy. The magnetocrystalline anisotropy with the martensitic transformation was enhanced, as in the case of other ferromagnetic shape memory alloys [27–29].

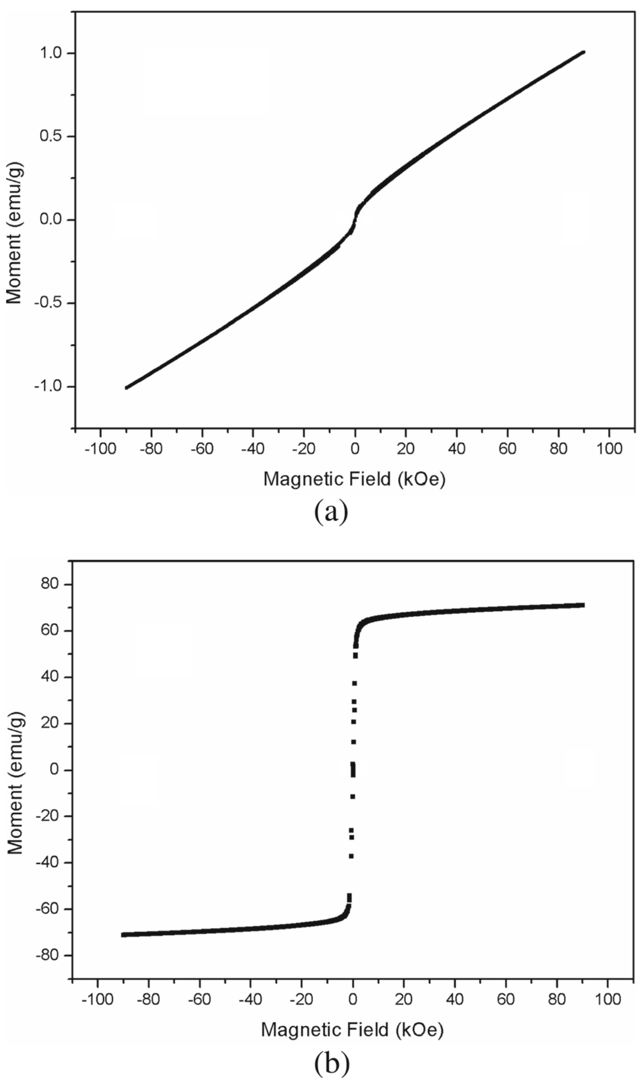


Fig. 2 Magnetization as a function of external magnetic field at $T = 300$ K. **a** CuAlMn alloy. **b** CuMnAl alloy

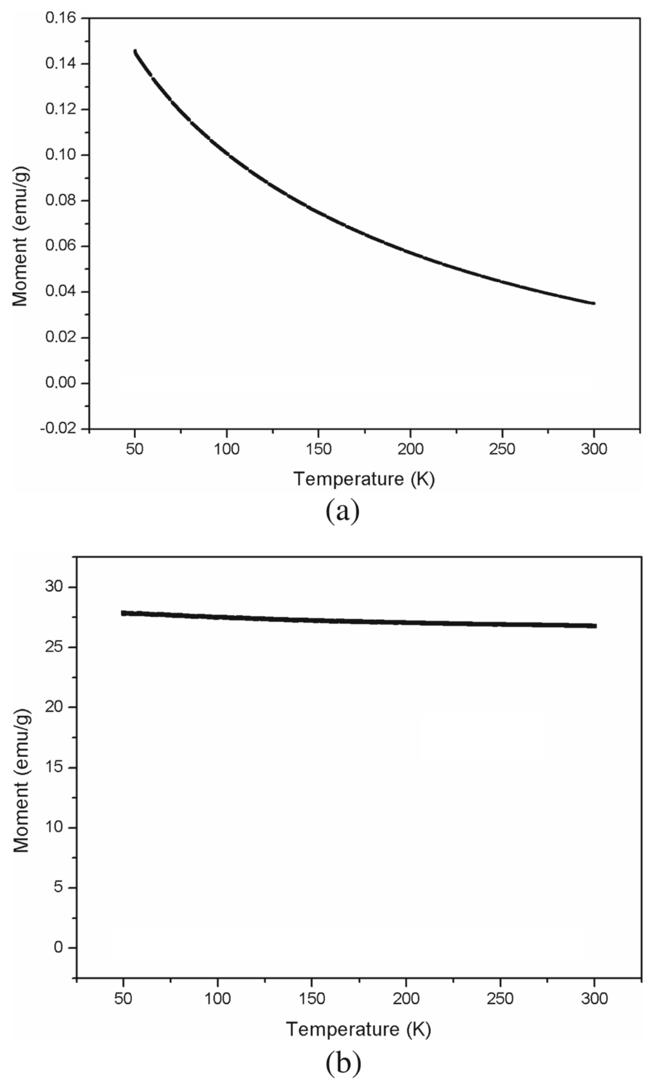


Fig. 3 The magnetization curves as a function of temperature between 50 and 300 K. **a** CuAlMn alloy. **b** CuMnAl alloy

Figure 4a and b shows the temperature dependence of magnetic susceptibility for CuAlMn and CuMnAl alloys in the temperature range from 0 to 300 K. The magnetic susceptibility values of the alloys were found to increase linearly with increasing temperatures. The magnetic susceptibility of the martensite and that of the austenite are different. Because the martensitic transformation is diffusionless and the number of Mn–Mn interactions does not change, the distances between them do [5]. The Mn–Mn distances may also differ in the martensite or in the β phase. The distances between the Mn–Mn pairs are important for magnetic susceptibility. Previous studies showed that nearest-neighbor Mn atom interactions are ferromagnetic [1, 5, 30–32]. Magnetic materials are generally classified into two main groups as hard and soft magnetic behaviors. The magnetic properties of materials can be affected by heat treatment, external stress, chemical composition, and small amounts of certain impurities. And also, coercivity, hysteresis losses, permeability, remanence, and magnetic stability are all regarded to be structure sensitive [33, 34]. Both the CuAlMn and CuMnAl alloys exhibited a typical soft magnetization behavior. This magnetic behavior is similar to that in both copper-based shape memory alloys and the other ferromagnetic shape memory alloys [1, 5, 34–37]. This would be considered as an amazing outcome of the present study.

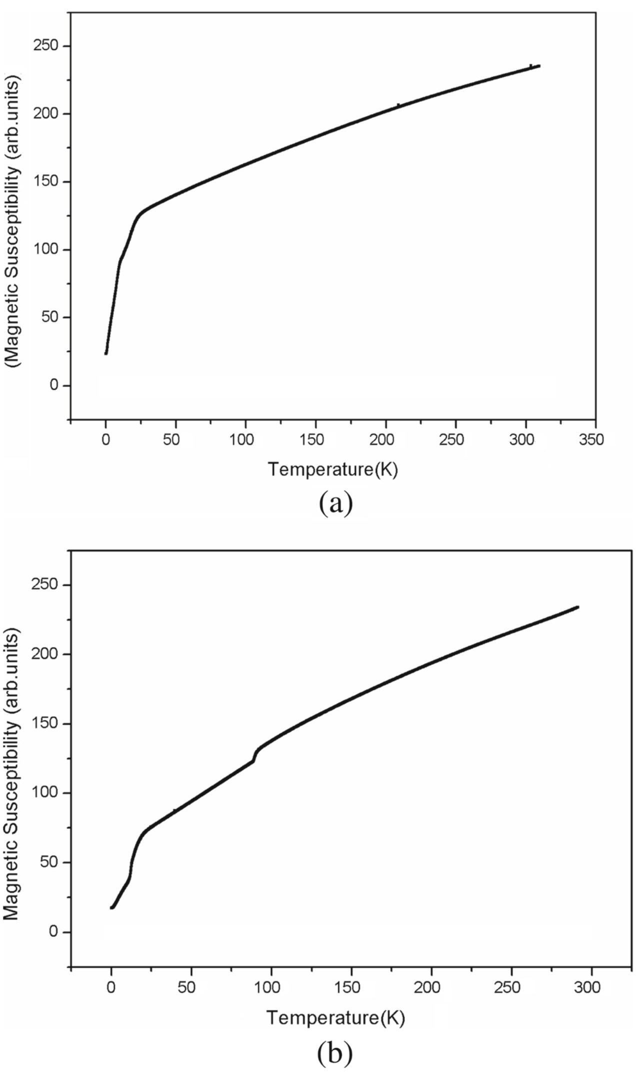


Fig. 4 The magnetic susceptibility (χ) curves as a function of temperature of **a** CuAlMn and **b** CuMnAl alloys

4 Conclusions

In this paper, the effect of a magnetic field on the properties of the CuAlMn and CuMnAl alloys was studied. The results of this study can be summarized as follows:

In the present study, the two types of martensite morphology formed in $Cu_{85.41}Al_{9.97}Mn_{4.62}$ alloy and austenite phase obtained in the $Cu_{82.41}Mn_{13.81}Al_{3.78}$ alloy. The CuAlMn and CuMnAl alloys are ferromagnetic even though its atomic constituents are all nonferromagnetic. The ferromagnetic properties of these alloys depend on the Mn–Mn interactions. This study showed the difference between the magnetization in the martensitic and that in the austenitic state. The coercivity values of these alloys are probably due to the different crystal structures. Both the CuAlMn and CuMnAl alloys exhibited a typical soft magnetization behavior. Soft magnetic materials are used extensively in technological application in power electronic circuits, inductors, and chokes.

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