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Martensitic transformation of Cu–10at.%Al–9at.%Ga–11at.%Mn ferromagnetic β alloy

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Abstract

The transformation behavior of Cu–Al–Ga–Mn alloy was investigated by differential scanning calorimetry, X-ray diffraction and vibrating sample magnetometer techniques. It was found that the Al substitution for Ga suppresses the formation of the ω phase which occurs to a great extent in the Cu–Ga–Mn ternary alloys.

Keywords: Cu–Al–Ga–Mn alloy; Shape memory alloys (SMA); Martensitic phase transformation; Magnetic properties; ω-phase

1. Introduction

Ferromagnetic shape memory alloys (FSMAs) have received a great deal of attention as high performance magnetically controlled solid-state actuator materials, since FSMAs such as the Ni–Mn–Ga system [1] were found to show a large magnetic field-induced strain by the rearrangement of the twin variant. To date, several FSMA candidates have been reported, including Fe–Pd [2], Fe–Pt [3] and some body-centered cubic ordered (bcc) alloy systems [4–6]. In particular, Oikawa et al. have conducted systematic studies of the martensitic transformation and magnetic transition in several bcc-ordered alloy systems [7–12] and have found that Co–Ni–Al [7], Co–Ni–Ga [9] and Ni–Fe–Ga [12] alloys as new types of alloy systems are promising FSMAs.

Very recently, the present authors reported the ferromagnetic shape memory properties of the Cu–Ga–Mn β ($L2_1$ Heusler structure) alloy system [13], where the alloys in the composition range of Cu–21at.% Ga–(13–15)at.%Mn show a thermoelastic martensitic transformation from $L2_1$ to 2H (γ': hcp) in the ferromagnetic state. Although the Cu–Ga–Mn β alloy system shows promise as a new FSMA, there is a significant problem in that Cu–Ga–Mn β alloys lose their shape memory properties during ageing at room temperature for only several hours because of precipitation of the ω phase. In the present study, an attempt was made to suppress the formation of the ω-phase at room temperature in Cu–Ga–Mn FSMAs by the substitution of Al for Ga. The martensitic and magnetic transformations of the Cu–10at.%Al–9at.%Ga–11at.%Mn alloy are reported herein.

2. Experimental procedures

Cu–10at.%Al–9at.%Ga–11at.%Mn and Cu–21at.% Ga–14at.%Mn alloys were prepared by induction

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melting under an argon atmosphere using pure copper (99.99%), aluminum (99.7%), gallium (99.999%) and manganese (99.9%). Some small pieces of the specimen taken from the ingot were sealed in a quartz capsule filled with argon gas. Solution treatment to prepare a homogeneous β single-phase alloy was conducted at 750 °C for 10 h and the specimen was then quenched in ice water. The martensitic transformation temperatures were determined by differential scanning calorimetry (DSC) with cooling and heating rates of 10 °C/min. The magnetization, M, at room temperature and magnetization vs. temperature (M–T) curves were measured by a vibrating sample magnetometer (VSM), M–T curves being obtained at 500 Oe with cooling and heating rates of 5 °C/min. The crystal structure of the martensite phase was identified by X-ray diffraction (XRD).

3. Results and discussion

3.1. Martensitic transformation temperatures and crystal structures

Fig. 1(a) and (b) respectively show the DSC curves of the Cu–Ga–Mn alloy specimen and the Cu–Al–Ga–Mn alloy specimen held at a temperature of 25 °C after quenching. Although an exothermic reaction was observed at several hundred minutes after quenching in the Cu–Ga–Mn ternary alloy specimen, as shown in Fig. 1(a), no exothermic reaction appeared in the Cu–Al–Ga–Mn quaternary alloy specimen, as shown in Fig. 1(b). This indicates that the substitution of Al for Ga in Cu–Ga–Mn ternary alloys is very effective in restraining the ω transition. This effect of Al may be explained as being due to the stabilization of the bcc-β phase or to a decrease of diffusivity of solutes resulting from the increase of the melting point by the addition of Al. Fig. 2(a) and (b) show the DSC curves and the martensitic transformation temperatures of the Cu–Al–Ga–Mn quaternary alloy. The temperatures are M_s martensitic transformation starting temperature, M_f martensitic transformation finishing temperature, A_s reverse martensitic transformation starting temperature and A_f reverse martensitic transformation finishing temperature (plotted against ageing time at room temperature). The martensitic transformations during heating and cooling, which are represented by the peak on the DSC curves, are clearly observed even after ageing for 6 days as shown in Fig. 2(a), while they are completely lost within several hours in the Cu–Ga–Mn ternary alloys [13]. Moreover, the martensitic transformation temperatures increase with increasing ageing time in the early stage, about 1 day as shown in Fig. 2(b), which may be caused by the chemical ordering of the β phase as well as the behavior in the Cu–Al–Mn alloy [14]. However, the transformation enthalpy which corresponds to the area of the peak on the DSC curves due to the martensitic transformation and the martensitic transformation temperatures decreases with further age-

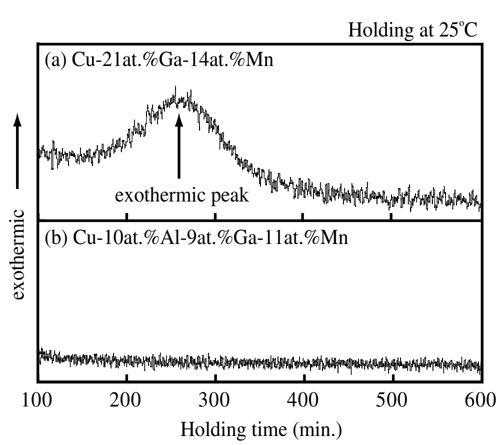

Fig. 1. DSC curves during holding at 25 °C of (a) Cu–Ga–Mn ternary alloy and (b) Cu–Al–Ga–Mn quaternary alloy, both quenched from 750 °C.

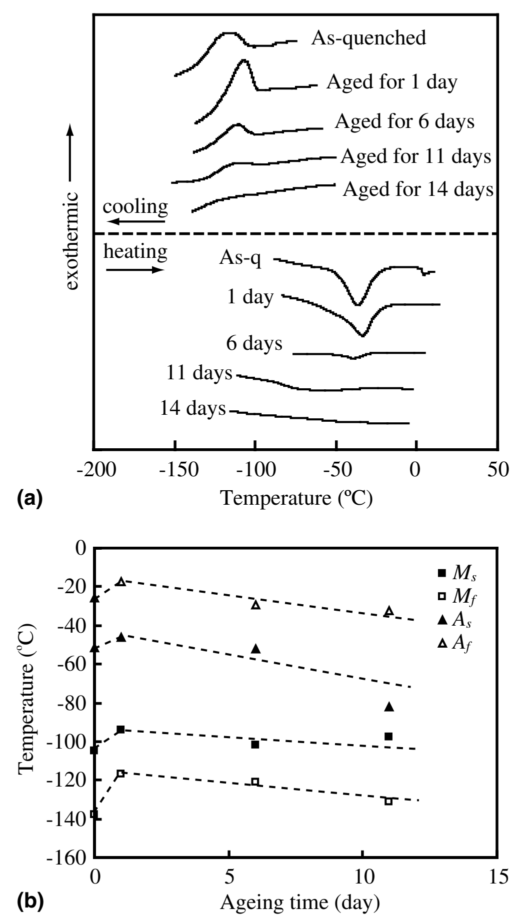

Fig. 2. Effect of the ageing time at 25 °C on martensitic transformation temperatures in Cu–10at.%Al–9at.%Ga–11at.%Mn quaternary alloy: (a) DSC curves and (b) martensitic transformation temperatures.