Phase Transformation and Magnetic Properties of Ferromagnetic Cu-Mn-Ga Alloys*1

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Phase transformation, microstructure and magnetic properties were investigated for Cu-(11-14) mol%Mn-20 mol%Ga. The structures of the magnetic domains were also investigated by Lorentz microscopy and electron holography. Plate-like martensite phase (C16, ordered hcp) was observed in as-quenched Cu-12 mol%Mn-20 mol%Ga. Phase transformation from C16 martensite to C12 phase (hcp) occurred at around 540 K on heating. The C16 phase decomposed into C12 (ordered hcp) and B2 (bcc) phase at around 700 K, then became the single B2 phase at around 840 K. By subsequent slow cooling, C12 phase was observed at room temperature. The results obtained from Lorentz microscopy and electron holography revealed that the twin plates of C16 martensite and the magnetic domain have one-to-one correspondence, suggesting high magneto-crystalline anisotropy energy of the martensite phase. The saturation magnetization and the Curie temperature increased with Mn content.

1. Introduction

Martensite phase of ferromagnetic shape memory alloys (FSMAs) exhibit a large strain by magnetic-field-induced twin reorientation with high response. Thus they are potential candidates for new actuator materials.

Ni-Mn-Ga alloys with Heusler structure has been studied most extensively by many researchers. Large field-induced strain was first demonstrated by Ullako et al.1) Maximum field induced strain around 10% was reported by Sozinov et al.2) For phase transformation behavior in Ni-Mn-Ga alloys, it was reported that the composition dependence of martensitic transformation temperature and the Curie temperature (Tc) can be rationalized by valence electron concentration (e/a); especially, the martensitic transformation temperature drastically increased by increasing e/a.3,4) Meanwhile, the Curie temperature is around 370 K and almost independent of e/a. Thus, search for new alloy systems that have the higher Curie temperature is necessary.

Cu-Mn-Al alloy is the most well-known Heusler alloy based on 3d-transition metal elements. The Curie temperature of Cu2MnAl is 603 K, higher than that of Ni-Mn-Ga alloys. Also, high Curie temperature may be achieved for Cu-Mn-Ga alloys, where Al replaces Ga in Cu-Mn-Al alloys. Hames et al. reported that Cu-15 mol%Mn-22.5 mol%Ga alloy quenched from 973 K is ferromagnetic and exhibits martensite-like microstructures at room temperature.5) Ternary phase diagrams of Cu-Mn-Ga alloys near the Cu corner were investigated by Baranchikov et al.6) Ternary phase diagram of Cu-Mn-Ga at 973 K and binary phase diagram of Cu-Ga alloy7) are shown in Fig. 1(a) and Fig. 1(b), respectively. It was found that at 973 K β phase (bcc structure, a = 0.32 nm) region exists around 20 mol%Ga and an increase of Mn content extends the β phase region as seen in Fig. 1(a). On cooling from the β phase state, the structure of Cu-Mn-Ga changes to ζ phase (hcp structure, a = 0.26 nm, c = 0.42 nm8)), and then to ζ' phase (DO19). Baranchikov also reported that Cu-Mn-Ga alloy quenched from β phase shows lamellar structure at room temperature. Massalski investigated massive transformation in Cu-Ga β alloys. He reported that Cu-Ga alloy quenched from β phase transforms to ζ phase, and martensite-like microstructure was observed with the increase of the cooling rate.9) Recently, Oikawa et al.10) reported that ferromagnetic martensite structure and thermoelastic martensitic transformation were observed in quenched Cu-(13-14) mol%Mn-21 mol%Ga. They also reported that martensitic transformation disappeared after aging at room temperature for 1 day.

In this study, phase transformation, microstructure and magnetic properties were investigated for Cu-(11-14) mol%Mn-20 mol%Ga.

2. Experimental Procedure

Polycrystalline ingots of Cu-(11-14) mol%Mn-20 mol%Ga were obtained by arc-melting method. The Cu-Mn-Ga alloys ingots were the homogenized in β phase state at 973 K for 259.2 ks, followed by water quenching. Energy dispersive X-ray spectroscopy (EDX) was carried out for all quenched ingots in order to assess the chemical compositions.

Surfaces of as-quenched samples were observed by optical microscope (OM) equipped with the Nomarski prism.

The phase transformation temperatures were measured with a RIGAKU DSC8230 differential scanning calorimeter (DSC). The measurement took place between 293–973 K temperatures for two cycles with a heating/cooling rate of 10 K/min.

*1This Paper was Originally Published in Japanese in J. Japan Inst. Metals 70 (2006) 849-855.
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 DOI: 10.2320/matertrans.MI200709

Received May 1, 2007; Accepted September 13, 2007; Published October 18, 2007

Keywords: ferromagnetic shape memory alloy, martensitic transformation, magnetic domain, twin

Special Issue on Structural and Functional Control of Materials through Solid-Solid Phase Transformations in High Magnetic Fields
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The temperature dependence of elastic modulus ($E'$) and the internal friction ($\tan \delta$) were measured with a NETZSCH DMA242C dynamic mechanical analyzer (DMA). The samples dimensions were $15 \times 5 \times 0.5$ mm. The vibration frequency, temperature range and heating/cooling rate were 10 Hz, 293–873 K and 5 K/min., respectively.

Transmission electron microscopy (TEM) was employed in order to assess the samples microstructure and to clarify its relation with the phase transformation. The observations were done for the as-quenched and heat treated samples between 563–973 K. The crystal structure of the samples was also evaluated with an RIGAKU RINT-2500X-ray diffractometer.

Magnetic domain structures were observed by the Lorentz microscopy and electron holography on a TEM JEOL JEM-3000F(300kV) equipped with a field-emission gun, a biprism and a special objective lens with a magnetic shield. The magnetic field at the specimen position was around 32 A/m. The measurements of the magnetization at room temperature and the Curie temperature ($T_C$) were carried out with vibrating sample magnetometer (VSM) TM-VSM261483-HGC. The applied external magnetic field varied from $-1.2$ to $1.2$ MA/m ($-15$–$15$ kOe).

To evaluate $T_C$, the temperature dependence of magnetization under an external field of 79.6 kA/m (1 kOe) was measured. The heating rate was 10 K/min.

3. Results and Discussion

An OM image of the as-quenched Cu-12.4 mol% Mn-20.2 mol% Ga sample is shown in Fig. 2. Plate-like morphology, typical of martensite phase, can be seen. A TEM bright field (BF) image and selected area diffraction (SAD) pattern of the as-quenched Cu-12Mn-20Ga are shown in Fig. 3. The martensitic twin structure is seen in the BF image. The corresponding SAD pattern is presented as an inset in Fig. 3. The main diffraction spots are indexed as $\zeta$ phase (hcp) and are accompanied by additional weak reflections at $\frac{1}{2} \{401\}$01 positions. This indicates that the martensite phase has an ordered hcp structure. Hereafter, it will be referred to as $\zeta_M$ phase.

The observation of the magnetic domain structures of $\zeta_M$ martensite in as-quenched Cu-12Mn-20Ga was carried out. The Lorentz micrographs of over-focus and under focus condition, a hologram obtained from electron holography, and a phase-reconstructed image are shown in Fig. 4. In Fig. 4(a) and (b), the martensite twin plates are seen. White or black lines at the correspondent location of the twin boundaries can be seen. Comparing Fig. 4(a) and (b),
it can be noted that black and white lines are reciprocally inverted in the two images. This contrast change indicates that the direction of magnetization changes the twin boundaries. Phase reconstructed image obtained from Fig. 4(c) is shown in Fig. 4(d). Bending of interference fringes are seen at the twin boundaries (Fig. 4(c)). Phase reconstructed image (Fig. 4(d)) confirms that the magnetization direction changes only at the twin boundaries, and the magnetization vectors are aligned parallel to a particular crystallographic orientation inside the twin plates. This suggests that $\xi_M$ martensite have high uniaxial magnetocrystalline anisotropy energy.\textsuperscript{11} The magnetic domain and twin plate have a one-to-one correspondence in $\xi_M$ martensite of Cu-Mn-Ga alloy, and the martensite may exhibit twinning magnetostriction if the twinning stress is sufficiently low.\textsuperscript{12,13} More detailed discussion of magnetocrystalline anisotropy and magnetostriction require the measurements using a single crystal.

DSC profiles of the first and second thermal cycles for as-quenched Cu-12Mn-20Ga alloy are shown in Fig. 5(a) and Fig. 5(b), respectively. In Fig. 5(a), a broad endothermic peak appeared around 540 K on heating. This endothermic peak originates from irreversible phase transformation since no correspondent peak is observed on cooling. At around 700 K, the DSC curve shows a smooth shoulder. Since no corresponding changes are observed on cooling curve, this change is also due to an irreversible transformation. Sharp peaks are observed at around 800–840 K on heating and cooling. These peaks appeared at almost same temperature on the second thermal cycle (Fig. 5(b)). This result indicates that these peaks originate from reversible transformation.

The temperature dependence of elastic modulus ($E'$) and internal friction ($\tan \delta$) is shown in Fig. 6. The DSC profile after the first heating cycle is also shown for comparison. It can be noticed that the changes in $E'$ and $\tan \delta$ reflect those observed in the heat flow. In Fig. 6, $E'$ slightly increases around 450–550 K. This change in $E'$ corresponds to the peak at 540 K on DSC profile. Moreover, $E'$ increases drastically at around 700 K and is accompanied by a slight increase in $\tan \delta$. The DSC profile also shows a step-like change at 700 K on heating. These changes indicate that crystal structure changes at 700 K. The DSC profiles exhibit a sharp endothermic peak at around 840 K on heating. In Fig. 6, $E'$ significantly decreases and $\tan \delta$ drastically

Fig. 4 Micrographs of the magnetic domain structures in as-quenched Cu-12Mn-20Ga: (a) Lorentz micrograph (over focus); (b) Lorentz micrograph (under focus) (c) electron hologram and (d) reconstructed phase image from (c).
increases at the same temperature. These changes suggest that phase transformation occurs around 840 K on heating.

The DSC and DMA results indicate that phase transformations occur at around 540, 700 and 840 K on heating. In order to assess the microstructural changes at 540, 700, 840 and below 840 K on second thermal cycle, TEM observation for samples after various heating/cooling cycles was conducted. Heating/cooling rate was set to 10 K/min and samples are heated to various temperatures, i.e., 563 K, 823 K, 973 K in the first cycle and to 823 K on the second cycle.

TEM BF image and SAD pattern of the sample heated up to 563 K are shown in Fig. 7. Plate-like microstructures are observed. Fundamental reflections can be seen as in the as-quenched sample shown in Fig. 3; however, the superlattice reflections did not appear at \( \frac{1}{2}q_{101} \) positions. It is suggested that after heating to 563 K the sample is in \( \gamma \) phase (hcp).

Lattice parameters of the \( \gamma \) phase determined from the XRD analysis are \( a = 0.26 \text{ nm} \) and \( c = 0.42 \text{ nm} \). The broad endothermic peak appeared around 540 K in DSC profile is thus due to the order-disorder phase transformation, i.e., disordering of \( \gamma \) martensite phase to \( \gamma \) phase.

The TEM bright field image of the sample heated up to 823 K is shown in Fig. 8(a). Elongated precipitates can be seen. The microstructures and compositions of the matrix and precipitates are shown in Fig. 8(b). Figure 8(c) shows the SAD pattern obtained from the encircled region in Fig. 8(b). The composition of the matrix is Cu-27 mol\%Mn-26 mol\%Ga, respectively. The SAD pattern indicates that the crystal structure of the matrix is disordered bcc (\( \beta \) phase), and the precipitate is hcp. However, the lattice parameters \( a \) and \( c \) are twice as large as those of the \( \gamma \) phase. This hcp structure is thus different from \( \gamma \) (D0\(_{19}\)) one. This phase is referred to as \( \gamma' \) hereafter. The orientation relationships between the matrix and the precipitates are \([2110]_{\gamma} \parallel [013]_{\beta} \) and \([0116]_{\gamma} \parallel [031]_{\beta} \). Thus the changes around 700 K shown in Fig. 5 and Fig. 6 correspond to the phase decomposition of \( \gamma \) phase to \( \beta \) and \( \gamma' \).

The TEM bright field image and SAD pattern of the sample heated up to 973 K are shown in Fig. 9. Many dislocations and stacking faults are observed. The SAD
pattern shows that the sample is \(\zeta\) phase and has hcp crystal structure at room temperature. It is suggested that the sample became \(\beta\) phase at 973 K and then a \(\beta \rightarrow \zeta\) phase transformation occurred during cooling.

The TEM bright field image and SAD pattern of the sample heated up to 823 K on the second thermal cycle are shown in Fig. 10. After the first heating cycle, elongated precipitates (\(\zeta''\) phase) were observed in the sample as shown in Fig. 8. However, microstructure shown in Fig. 10 does not contain any \(\zeta''\) phase. Moreover, its features are almost same as those exhibited by the sample heated up to 973 K and shown in Fig. 9. The SAD pattern shows same \(\zeta\) phase spots as well. The microstructure and the SAD pattern of the sample after heating to 973 K on the second thermal cycle are shown in Fig. 11. These results indicate that the sample is \(\zeta\) phase at room temperature. Only a pair of peaks around 800−840 K was observed in the DSC profiles at the second thermal cycle. Results of DSC measurements and TEM observation indicate that 973 K reversible \(\zeta\)-\(\beta\) phase transformation occurs after first thermal cycle up to 973 K.
Schematic image of the phase transformation behaviour on Cu-12Mn-20Ga alloy is shown in Fig. 12. The microstructure of the sample heated to 973 K consists in $\beta$ phase. It transforms into $\zeta_M$ martensite after quenching. $\zeta_M$ martensite has ferromagnetic property and shows twin plates. On heating, order-disorder $\zeta_M \rightarrow \zeta$ phase transformation occurs around 540 K. Then $\zeta$ phase is distributed to $\zeta'$ and $\beta$ phase around 700 K. Finally single $\beta$ phase can be obtained at high temperature. $\beta$-$\zeta$ phase transformation occurs on slow cooling. After the first thermal cycle, $\zeta$-$\beta$ massive transformation occurs. $\zeta_M$ martensite phase is a specific phase of quenching. Additionally, the phase transformation behaviours of the first and second thermal cycle are significantly different. It is suggested that the difference between transformation behaviour of the first and second thermal cycle is related to the excess of vacancies produced by quenching. However, a more detailed investigation concerning this point is under work.

To confirm shape memory effect, a plate sample was rapidly heated by a small gas burner after bending to temperatures above 573 K. Shape recovery was observed. Thus it is inferred that the alloys undergo martensitic transformation and reverse transformation by quenching and rapid heating.

The magnetization measurements at room temperature and the Curie temperature measurements were carried out for Cu-(11-14) mol% Mn-20 mol% Ga alloys. The magnetization at 1.2 MAm$^{-1}$ ($M$) and the Curie temperature ($T_C$) are plotted as a function of Mn content ($C_{Mn}$) in Figs. 13(a) and (b), respectively. Cu-11 mol% Mn-20 mol% Ga alloy exhibited a paramagnetic-like magnetization curve without saturation and a low value of $M$. However, $M$ was significantly higher and the magnetization curve indicated clear saturation in Cu-12 mol% Mn-20 mol% Ga. $M$ increases with the Mn content and the maximum value of the $M$ was about 30 Am$^2$/kg for Cu-14 mol% Mn-20 mol% Ga. As shown in Fig. 13(b), the Curie temperatures of all Cu-Mn-Ga alloys used in the present study were above 400 K, and the highest $T_C$ of 474 K was
achieved in the 14 mol%Mn alloy. The 11 mol%Mn alloy exhibited only a minor change in magnetization during heating and the corresponding data was plotted as an open circle. After the Curie temperature measurements the samples became paramagnetic. This may be due to the $\zeta$-$\beta$ phase transformation occurred during the heating/cooling cycle of the Curie temperature measurements.

4. Conclusion

In the present study, the phase transformation behaviour was investigated. Cu-12Mn-20Ga alloy becomes $\zeta_M$ martensite phase after quenching from 973 K. $\zeta_M$ martensite has ferromagnetic properties and high magneto-crystalline anisotropy. The $\zeta_M$-$\zeta$ and the $\zeta$-$($$\zeta''+\beta$$)$ phase transformations occur upon heating with a 10 K/min. rate. Then single $\beta$ phase is obtained at high temperature. $\beta$-$\zeta$ phase transformation occurs during cooling and then $\zeta$-$\beta$ massive transformation occurs after the first thermal cycle.

The magnetization increases with Mn content, and the maximum value is about 30 Am$^2$/kg under an applied filed of 1.2 MAm$^{-1}$. The Curie temperature also increases with Mn content. The Curie temperature for Cu-12 mol%Mn-20 mol%Ga is around 440 K, which was significantly higher than that in Ni-Mn-Ga ferromagnetic shape memory alloy.

Acknowledgement

A part of this research was supported by Toyoaki Research foundation.

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