



Structure and Magnetic Properties of Cu Doped MnAl

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Authors' contributions

This work was carried out in collaboration between all authors. Authors HXW and PZS prepared the samples and wrote the first draft of the manuscript. Authors WJ, XFX, MZ, ZFL and HLG analyzed the structure and magnetic properties of the samples. Authors JGL and CJC did help in designing the study. All authors read and approved the manuscript.

Original Research Article

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ABSTRACT

The effects of Cu-doping and heat-treatment on the structure and magnetic properties of δ -MnAl have been investigated. Copper stabilizes the structure of δ -MnAl and enhances the fraction of δ -phase while excess Cu (≥ 9 at%) results in the formation of more α - and/or β -phase. In comparison with the binary Mn-Al system, the Cu-doped ternary alloy is more insensitive to heat-treatment in structural transformation. Cu-doping usually decreases the saturation magnetization while a certain amount of Cu enhances the coercivity of the samples. The annealing time and temperature have a substantial effect on the magnetic properties of MnAl.

Keywords: Magnetic properties; MnAl; structure; Cu substitution.

1. INTRODUCTION

The development of rare-earth-free permanent magnets is becoming more important with increasing cost and decreasing reserve of rare earth resources. The MnAl-based permanent

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magnets have attracted continuous attention since its discovery in 1958 for its low cost and attractive magnetic performance superior to conventional hard ferrites and Alnicos [1]. A number of phases with varied structures have been reported in Mn-Al binary alloys [2,3]. The δ -phase of Mn-Al is most important for use as hard-magnet. However, it is difficult to obtain the pure meta-stable δ -phase. The magnetic binary alloy was usually produced by cooling the sample at a rate of 10 K/min [4], or by quenching the high temperature α -phase to room temperature with subsequent isothermal annealing at temperatures between 723 K and 973 K for a short while [5]. In order to stabilize the meta-stable δ -MnAl and increase the fraction of δ -phase in the samples, the doping effect of several elements, including Ti, Ni, C, B and Zn has been studied [4,6-8]. Carbon or zinc could stabilize the δ -MnAl [7,8]. In this work we investigated the effect of Cu addition on the structure and magnetic properties of the Mn-Al binary system.

2. EXPERIMENTAL DETAILS

High purity (>99.9%) Mn, Al and Cu in nominal composition of $Mn_{54}Al_{46}$, $Mn_{54}Al_{43}Cu_3$, $Mn_{54}Al_{40}Cu_6$, $Mn_{54}Al_{37}Cu_9$ were melted by induction melting in an argon atmosphere. Then the melt was quenched in water. After that the $Mn_{54}Al_{43}Cu_3$ quenched ingots were annealed in vacuum at 420°C for 10 min, 20 min, 30 min, 60 min and 90 min, respectively. The as-quenched $Mn_{54}Al_{43}Cu_3$ ingot was milled in kerosene for 10h. $Mn_{54}Al_{40}Cu_6$ and $Mn_{54}Al_{37}Cu_9$ quenched ingots were annealed in vacuum at 420°C for 20 min, 40 min and 60 min respectively. The structure of the samples was determined by using a powder x-ray diffractometer (XRD) with Cu K_α radiation in a step size of 0.02° and a sweep rate of 4°/min. The magnetic properties of the samples were measured by using a Vibrating Sample Magnetometer (VSM) with a vibration frequency of 50 Hz and in magnetic field up to 1.5 T.

3. RESULTS AND DISCUSSION

3.1 Structure Characterization

The x-ray powder diffraction patterns of the samples are shown in Fig.1. The XRD patterns for the original $Mn_{54}Al_{46}$ water quenched samples are shown in Fig. 1 (a), which could be mainly indexed with α -MnAl and a small amount of $\tilde{\alpha}$ and δ phase, the peaks of α -MnAl and δ -MnAl overlap at $2\theta=41.22^\circ$. The broadening of these diffraction peaks indicates tiny crystalline size of these phases in the sample. The x-ray powder diffraction pattern of the water quenched $Mn_{54}Al_{43}Cu_3$ is shown in Fig.1 (b), which could be indexed with δ -phase as the major phase, indicating substantial enhancement of the formation of the δ -phase resulting from Cu doping. Fig. 1 (c) shows the XRD patterns of the $Mn_{54}Al_{43}Cu_3$ after ball-milling. A broadened peak for $\tilde{\alpha}$ -phase could be seen in Fig. 1 (c), indicating a transformation of the δ -phase to a more stable Al-rich $\tilde{\alpha}$ -phase. Figs 1(d)-(f) show the effect of annealing time on the phase transformation in $Mn_{54}Al_{43}Cu_3$, which is mainly composed of δ phase. No substantial effect of annealing time on the structure was detected. By comparing Figs. 1(b), (d)-(f), we could see that the diffraction peaks for δ -MnAl almost has no change, indicating beneficial effect of Cu-substitution and heat-treatment on the formation of the δ -phase. It is known that the transformation of α -MnAl to δ -MnAl in doping-free binary alloys is sensitive to annealing time and temperatures, however, our results indicate that the phase transformation become insensitive in Cu-doped ternary samples, owing to the structural stabilizing effect of Cu-doping.

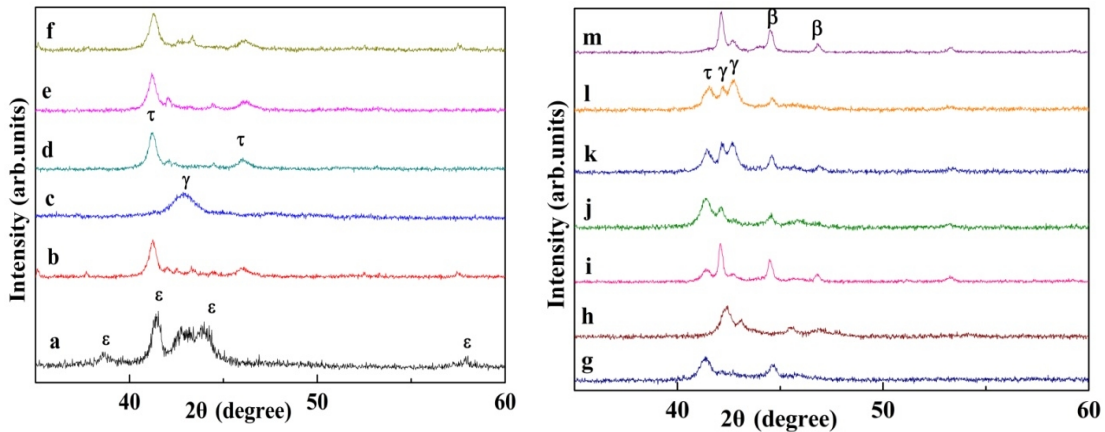


Fig. 1. XRD patterns of (a) $Mn_{54}Al_{46}$, (b) $Mn_{54}Al_{43}Cu_3$, (c) $Mn_{54}Al_{43}Cu_3$ milled for 10 h, (d, e, f) $Mn_{54}Al_{43}Cu_3$ treated at 420°C for 10, 20, 30 min, respectively, (g, h, i, j) $Mn_{54}Al_{40}Cu_6$ treated at 420°C for 0, 20, 40, 60 min, respectively, (k, l, m) $Mn_{54}Al_{37}Cu_9$ treated at 420°C for 0, 20, 40 min, respectively. The symbols of δ , \tilde{a} , \tilde{a} , and \tilde{a} represent the phases with same names

Figs. 1 (g)-(j) show the XRD patterns of the $Mn_{54}Al_{40}Cu_6$ annealed at 420°C for 0, 20, 40, 60 min respectively. The δ -phase is the major phase in the as-quenched $Mn_{54}Al_{40}Cu_6$, as shown in Fig. 1 (g). For $Mn_{54}Al_{40}Cu_6$ annealed at 420°C for 20 min, the major phase is \tilde{a} -phase, as shown in Fig. 1 (h). For $Mn_{54}Al_{40}Cu_6$ annealed for 40 min and 60 min, the relative intensity of the diffraction peaks for δ -phase and \tilde{a} -phase is almost the same, suggesting coexistence of these two phases.

Fig. 1(k - m) show the XRD patterns of the $Mn_{54}Al_{37}Cu_9$ annealed at 420°C for 0, 20, 40 min, respectively. It was observed that \tilde{a} -phase Mn-Al is the major phase. The diffraction peaks for \tilde{a} -phase become stronger with increasing annealing time as seen in curve k, l and m. For samples annealed for 40 min, the diffraction peaks for δ -phase disappeared.

Based on the above discussions, we could see that the Cu content substituted to Al has a significant effect on the phase formation process. Cu-substitution can stabilize the structure of the δ -phase. However, excess Cu (≥ 9 at%) would result in the formation of more \tilde{a} -phase.

3.2 Magnetic Properties

Fig. 2(a) shows the effect of heat-treatment time on the magnetic properties of $Mn_{54}Al_{43}Cu_3$. The coercivity of the samples is increasing with increasing heat treatment time. The saturation magnetization is increasing first and then decreasing with increasing heat treatment time. A saturation magnetization of 70.7 Am²/kg was observed when the heat treatment time was 30min. The increasing saturation magnetization with increasing heat treatment time was ascribed to the structural stabilizing effect of Cu on ferromagnetic δ -MnAl and its presence as major phase in the samples. In comparison with heat-treated samples, water-quenched sample exhibit a lower coercivity and saturation magnetization. Heat treatment has a substantial effect on the magnetic properties of the samples.

The effect of heat treatment time on the magnetic properties of $Mn_{54}Al_{40}Cu_6$ is shown in Fig. 2(b). It is seen that the coercivity decreases while the saturation magnetization increase first and then decrease with increasing annealing time.

Different from the results of $Mn_{54}Al_{43}Cu_3$ as seen in Fig. 2(a), the decreasing coercivity of $Mn_{54}Al_{40}Cu_6$ with annealing time as shown in Fig. 2(b) indicates that excess Cu is detrimental to the magnetic properties. The saturation magnetization is decreasing significantly after 60 min annealing, while increasing slightly within 20 min for unknown reason.

Fig. 2(c) shows the effect of heat treatment time on the magnetic properties of $Mn_{54}Al_{37}Cu_9$. The coercivity of the samples is increasing first and then decreasing with increasing heat treatment time, the saturation magnetization decreases almost linearly with annealing time. In summary, Fig. 2 shows that the annealing time has a substantial effect on the magnetic properties of the samples.

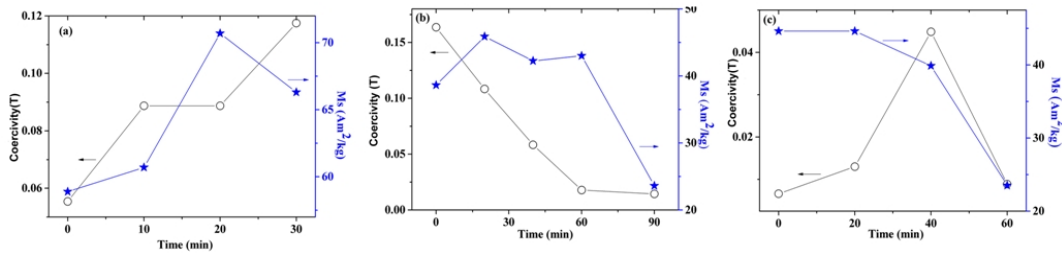


Fig. 2. The effect of annealing time on the coercivity and saturation magnetization of (a) $Mn_{54}Al_{43}Cu_3$; (b) $Mn_{54}Al_{40}Cu_6$, and (c) $Mn_{54}Al_{37}Cu_9$. The samples were annealed at 420°C

The effect of Cu content on the magnetic properties of $Mn_{54}Al_{46}$, $Mn_{54}Al_{43}Cu_3$, $Mn_{54}Al_{40}Cu_6$, $Mn_{54}Al_{37}Cu_9$ and $Mn_{54}Al_{34}Cu_{12}$ is shown in Fig. 3. In general, the Cu-substitution is detrimental to the saturation magnetization. The coercivity decreases with increasing Cu content to 3 at.% and then increases with continuous increasing Cu content to 6 at.%. The maximum coercivity was observed in $Mn_{54}Al_{40}Cu_6$.

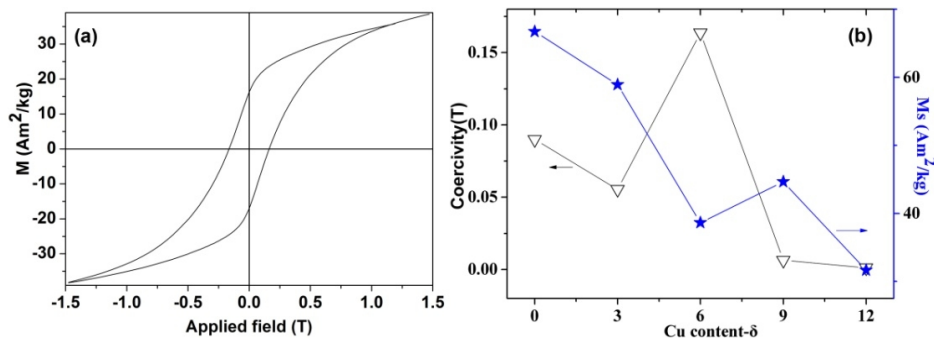


Fig. 3. (a) The typical magnetic hysteresis loops of $Mn_{54}Al_{40}Cu_6$. (b) The effect of Cu substitution to Al on the coercivity and saturation magnetization of $Mn_{54}Al_{46-\delta}Cu_{\delta}$ ($\delta=0, 3, 6, 9$)

4. CONCLUSION

In summary, the effect of Cu substitution and heat-treatment on the structure and magnetic properties of δ -MnAl has been investigated systematically. It was found that a certain amount of Cu doping could stabilize the structure of δ -MnAl and thus an enhanced fraction of δ -phase in the alloys could be produced. However, excess Cu would result in the formation of more β -phase and/or α -phase. In comparison with the doping-free Mn-Al system, the Cu-doped system is more insensitive to the heat-treatment. A certain amount of Cu substitution could enhance the coercivity of the samples. The Cu-doping usually results in a decrease of the saturation magnetization. The annealing time and temperature has a substantial effect on the magnetic properties.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

REFERENCES

1. Kono H. On the ferromagnetic phase in manganese-aluminum system. J. Phys. Soc. Japan. 1958;13:1444-51.
2. Yanar C, Wiezorek JMK, Radmilovic V, Soffa WA. Massive transformation and the formation of the ferromagnetic L10 phase in manganese-alumium based alloys, Metall. Mater. Trans. A. 2002;33:2413-23.
3. McAlister AJ, Murray JL. The (Al-Mn) aluminum-manganese system, Bulletin of Alloy Phase Diagrams. 1987;8:438-47.
4. Zeng Q, Baker I, Cui JB, Yan ZC. Structural and magnetic properties of nanostructured Mn-Al-C magnetic materials, J. Magn. Magn. Mater. 2007;308:214-26.
5. Hoydick DP, Palmiere EJ, Soffa WA. Microstructural development in MnAl-base permanent magnet materials: new perspectives, J. Appl. Phys. 1997;81:5624-6.
6. Sakka Y, Nakamura M, Koshimoto K. Rapid quenching and properties of hard magnetic materials in MnAl-X (X = Ti, Cu, Ni, C, B) systems, J. Mater. Sci. 1989;24:4331-8.
7. Dreizler WH, Menth A. Transformation kinetics of the ferromagnetic alloy Mn-Al-C, IEEE Trans. Magn. 1980;16:534-6.

8. Wang HX, Si PZ, Jiang W, Liu JJ, Lee JG, Choi CJ, et al. Structural stabilizing effect of Zn substitution on MnAl and its magnetic properties. *Open J. Microphysics*. 2011;1(2):19-22.

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