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Structural Stabilizing Effect of Zn Substitution on MnAl and Its Magnetic Properties

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Abstract

The effect of Zn substitution on the structure and magnetic properties of τ-MnAl has been investigated systematically. It is found that Zn substitution can stabilize the structure of τ-phase and thus a significant amount of τ-phase can be produced. Zn increases the coercivity and saturation magnetization of the τ-MnAl but reduces the Currie temperature. However, excess Zn is detrimental to the magnetic parameters. The optimum magnetic performance was found in samples with Zn substitution to 2.9% Mn atoms and 3.5% Al atoms, respectively.

Keywords: MnAl, Magnetic Property, Zn Substitution

1. Introduction

The development of rare earth free permanent magnets is becoming more and more important with increasing cost and decreasing reserve of rare earth resources. Ferromagnetic τ-MnAl, as a low cost rare-earth-free magnet, has received continuous attention since its discovery in 1958 for its superior magnetic performance in comparison with magnetically hard ferrites and Alnicos [1-3]. The τ-MnAl has a Currie temperature of 661 K, a manganese moment of 1.94 μ_B, and an enhanced magnetic anisotropy. The structure of ferromagnetic τ-MnAl is tetragonal, which can be interpreted to arise from a non-magnetic cubic structure by two subsequent steps, namely an electronic distortion due to spin polarization followed by a structural distortion into the tetragonal system [4]. Since the τ-MnAl is metastable, it is difficult to obtain pure phase of τ-MnAl, which usually is produced by a rapid quench of the high temperature ε-phase followed by isothermal annealing at temperatures between 400°C and 700°C for a short while, or by cooling the τ-phase at a rate of 10°C/min [2]. Long time annealing would result in decomposition of the τ-phase to the equilibrium γ-phase and β-phase. In order to stabilize the

τ-MnAl, the doping effect of several elements, including Ti, Cu, Ni, C, B, etc., has also been studied [2,5]. It was found that the addition of carbon to MnAl can stabilize the τ-phase [6,7]. Reports on the partial substitution of Mn in MnAl by Ni or Co could also be found [8,9]. The effect of introducing other elements into MnAl system has not been studied. The purpose of this work is to investigate the effect of doping Zn on the structure and magnetic properties of the Mn-Al system.

2. Experiments

High purity (>99.9%) Mn, Al and Zn in nominal composition of $Mn_{54}Al_{46-\delta}Zn_\delta$ (δ = 0, 1.6, 3.3, 4.7, 5), $Mn_{53.5}Zn_{0.5}Al_{46}$, $Mn_{53.4}Zn_{1.6}Al_{46}$, $Mn_{51.8}Zn_{3.2}Al_{46}$, and $Mn_{49}Zn_5Al_{46}$ were melted by using induction meting in an argon atmosphere. Then the melt was quenched in water. After that the quenched ingots were annealed at 420°C for 1 h in vacuum, respectively. The structure of the samples was determined by using a powder x-ray diffractometer (XRD) with Cu K_α radiation while the magnetic properties were measured by using a Vibrating Sample Magnetometer (VSM) in fields up to 1.5 T. Thermal analysis on the samples was carried out in argon atmosphere with a

temperature sweep rate of 20˚C/min.

3. Results and Discussion

The x-ray powder diffraction patterns of the $Mn_{54}Al_{46-\delta}Zn_{\delta}$ ($\delta = 0$, 1.6, 3.3, 5) water quenched samples and their counterparts after 420˚C and one hour vacuum heat-treatment are shown in **Figure 1**, respectively. The XRD patterns for the as-quenched $Mn_{54}Al_{46}$, as shown in **Figure 1(a)**, could be mainly indexed with orthorhombic ε-MnAl phase, which is stable at temperatures above 870˚C and is maintained to room temperature during quench. The weak broadened peak in the vicinity of 43˚ indicates the presence of γ and/or β-phase as minor phase in the sample. **Figure 1(b)** shows that the heat-treatment to $Mn_{54}Al_{46}$ induces the transformation of ε-phase to a more stable Al-rich γ-phase and Mn-rich β-phase. The diffraction peaks for meta-stable τ-phase could also be found but are very weak. Strong diffraction peaks appear in both water-quenched and heat-treated $Mn_{54}Al_{44.4}Zn_{1.6}$, as shown in **Figures 1(c)** and **(d)**, indicating stabilizing effect of Zn on the structure of τ-phase. Trace amount of ε-phase, β-phase and γ-phase are detected in the as-quenched $Mn_{54}Al_{44.4}Zn_{1.6}$. After heat-treatment, the ε-phase disappears while the diffraction intensity of β- and γ-phase made almost no change, indicating a phase transformation of ε-phase to τ-phase during heat-treatment. For $Mn_{54}Al_{42.7}Zn_{3.3}$, the τ-phase presents in the as-quenched samples but disappears after heat-treatment, as seen in **Figures 1 (e)** and **(f)**. These phenomena indicate that the τ-phase formed in $Mn_{54}Al_{44.4}Zn_{1.6}$ is more stable than that formed in $Mn_{54}Al_{42.7}Zn_{3.3}$. With increasing Zn content, the τ-phase, β-phase and γ-phase coexists in both water-quenched and heat-treated $Mn_{54}Al_{41}Zn_{5}$ samples as seen in **Figures 1(g)** and **(h)**.

It should be noted that for sample with $\delta = 1.6$, τ-phase is the major phase while for other samples β-phase is the major one. This result indicates that substitution of a certain amount of Zn to Al is beneficial for the formation of τ-phase. We speculate that atomic size may play an important rule in this process. It is known that the atomic size of Zn is slightly smaller than that of Al. Since the minimum internal energy in MnAl occurs very close to $c/a = 1$ (c and a are the lattice parameters), thus the tetragonal τ-phase is reported to be meta-stable [4]. When a small number of Al atoms were substituted by smaller Zn, a local lattice distortion that make tetragonal τ-phase more stable might occur to maintain internal energy minimum. However, for samples with increasing substitution $\delta \geq 3.3$, β-phase rather than ε or τ-phase formed as major phase in water quenched samples. Since β-phase is very stable and thus the heat-treatment has little effect on the structure of these samples.

Figure 2 shows the effect of Zn substitution to Al on the magnetic properties of $Mn_{54}Al_{46-\delta}Zn_{\delta}$ ($\delta = 0$, 1.6, 3.3, 5). For heat-treated samples, the coercivity and the saturation magnetization increase first and then decrease with increasing Zn substitution to Al. A maximum coercivity of 0.157 T was observed in heat-treated $Mn_{54}Al_{44.4}Zn_{1.6}$. The 0.157 T coercivity in our Mn-Al-Zn system is lower than the 0.34 T coercivity as reported in the Mn-Al-C samples [7]. Since the parameter of coercivity is very sensitive to microstructures, we tend to believe that certain partial substitution of Zn to Al might result in the formation of localized lattice defects that hinder magnetization reversal. The increasing saturation magnetization with Zn substitution was ascribed to the structural stabilizing effect of Zn on ferromagnetic τ-MnAl and its presence as major phase in the samples. Excess Zn would result in the formation of more β-phase and γ-phase that are detrimental to the magnetic performance. In comparison with heat-treated samples, most water-quenched samples exhibit a lower coercivity except $Mn_{54}Al_{42.7}Zn_{3.3}$, as seen in **Figure 2**. However, for samples with $\delta \geq 3.3$, the effect of heat-treatment on the coer-

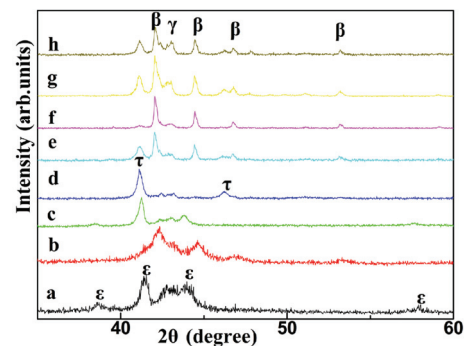**Figure 1. XRD patterns for (a) $Mn_{54}Al_{46}$, (b) Heat-treated $Mn_{54}Al_{46}$, (c) $Mn_{54}Al_{44.4}Zn_{1.6}$, (d) Heat-treated $Mn_{54}Al_{44.4}Zn_{1.6}$, (e) $Mn_{54}Al_{42.7}Zn_{3.3}$, (f) Heat-treated $Mn_{54}Al_{42.7}Zn_{3.3}$, (g) $Mn_{54}Al_{41}Zn_{5}$, and (h) Heat-treated $Mn_{54}Al_{41}Zn_{5}$. The heat-treatment for sample (b), (d), (f), and (h) was carried out in vacuum under 420˚C for one hour.**

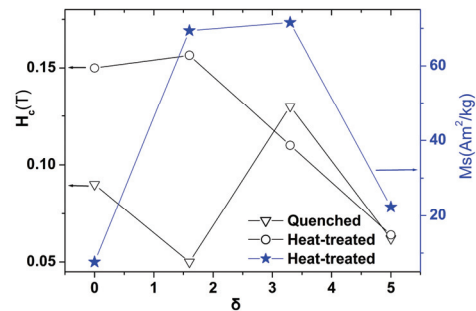**Figure 2. The effect of Zn substitution to Al on the coercivity and saturation magnetization of $Mn_{54}Al_{46-\delta}Zn_{\delta}$ ($\delta = 0$, 1.6, 3.3, 5).**

civity is decreasing due to the presence of stable β-phase and γ-phase in the samples. Heat-treatment has a strong effect on the magnetic properties of $Mn_{54}Al_{44.4}Zn_{1.6}$.

Figure 3 shows the XRD patterns of the water-quenched and the heat-treated ingots of $Mn_{53.5}Zn_{0.5}Al_{46}$, $Mn_{53.4}Zn_{1.6}Al_{46}$, $Mn_{51.8}Zn_{3.2}Al_{46}$, and $Mn_{49}Zn_5Al_{46}$. It is interesting that τ-phase formed in all water-quenched samples, indicating a strong structural stabilizing effect of Zn substitution to Mn on τ-MnAl. However, the β-phase and γ-phase were also formed in all samples during water-quench. For $Mn_{53.5}Zn_{0.5}Al_{46}$, as seen in **Figures 3(a)** and **(b)**, by comparing the relative diffraction intensity of τ-phase and β-/γ-phase, we noticed that the amount of τ-phase increased after heat-treatment. **Figures 3(c)** and **(d)** shows that the heat-treatment has little effect on the structure of $Mn_{53.4}Zn_{1.6}Al_{46}$. For $Mn_{51.8}Zn_{3.2}Al_{46}$, ε-phase was detected in water-quenched sample while it disappears after heat-treatment, as shown in **Figures 3(e)** and **(f)**. The intensity of τ-phase peaks were enhanced after heat-treatment, indicating a $\varepsilon \rightarrow \tau$ transformation in this process. **Figures 3(g)** and **(h)** shows that both water-quenched and heat-treated $Mn_{49}Zn_5Al_{46}$ were composed of τ-phase, β-phase and γ-phase, while heat-treatment had almost no effect on the structure. **Figure 3** shows that no pure τ-phase could be obtained in Zn substituting Mn process, for comparison **Figures 1(c)** and **(d)** shows that pure τ-phase could be obtained in Zn substituting Al process.

The effect of Zn substitution to Mn on the magnetic properties of $Mn_{54}Al_{46}$, $Mn_{53.5}Zn_{0.5}Al_{46}$, $Mn_{53.4}Zn_{1.6}Al_{46}$, $Mn_{51.8}Zn_{3.2}Al_{46}$ and $Mn_{49}Zn_5Al_{46}$ are shown in **Figure 4**. Both the saturation magnetization and the coercivity of the heat-treated samples increase first and then decrease with increasing Zn content. The maximum coercivity was observed in $Mn_{53.5}Zn_{0.5}Al_{46}$ while the maximum saturation magnetization was observed in $Mn_{53.4}Zn_{1.6}Al_{46}$. The enhancement of the magnetic performance for samples with lower Zn substitution indicates that Zn is beneficial for the formation of τ-phase. However, **Figure 4** also shows that higher Zn substitution is detrimental to the magnetic properties, suggesting a limited effect of Zn addition. It is interesting to note that heat-treatment increases the coercivity when Zn substitution is low and decreases the coercivity when Zn content is high.

Figure 5 plots the M-T and ΔT-T curves for the samples. The Currie temperature of $Mn_{54}Al_{42.7}Zn_{3.3}$, $Mn_{54}Al_{44.4}Zn_{1.6}$, $Mn_{53.5}Zn_{0.5}Al_{46}$ determined by using dM/dT method is in the vicinity of 371K-373 K, which is lower than the 388 K reported for τ-MnAl[3]. The result indicates that Zn substitution reduces the Currie temperature of τ-MnAl. The endothermal peak observed in **Figure 5(d)** was ascribed to the ferromagnetic-paramagnetic transition of τ-MnAl in $Mn_{54}Al_{42.7}Zn_{3.3}$.
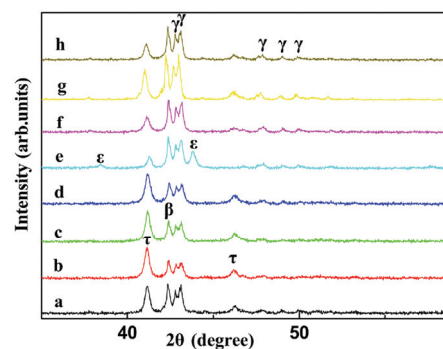

Figure 3. XRD patterns for (a) $Mn_{53.5}Zn_{0.5}Al_{46}$, (b) Heat-treated $Mn_{53.5}Zn_{0.5}Al_{46}$, (c) $Mn_{53.4}Zn_{1.6}Al_{46}$, (d) Heat-treated $Mn_{53.4}Zn_{1.6}Al_{46}$, (e) $Mn_{51.8}Zn_{3.2}Al_{46}$, (f) Heat-treated $Mn_{51.8}Zn_{3.2}Al_{46}$, (g) $Mn_{49}Zn_5Al_{46}$, and (h) Heat-treated $Mn_{49}Zn_5Al_{46}$. The heat-treatment for sample (b), (d), (f), and (h) was carried out in vacuum under 420°C for one hour.

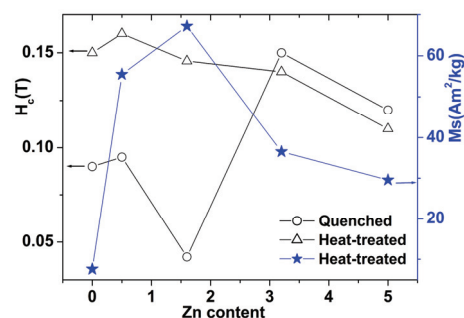**Figure 4. The effect of Zn substitution to Mn on the magnetic properties of $Mn_{54}Al_{46}$, $Mn_{53.5}Zn_{0.5}Al_{46}$, $Mn_{53.4}Zn_{1.6}Al_{46}$, $Mn_{51.8}Zn_{3.2}Al_{46}$ and $Mn_{49}Zn_5Al_{46}$.**
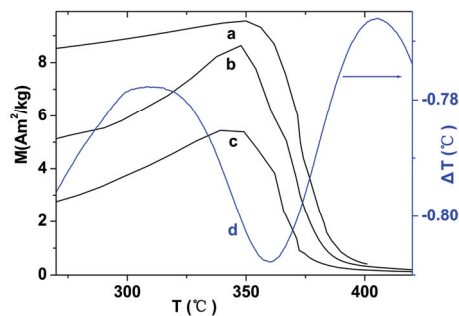

Figure 5. Temperature dependence of magnetization of heat-treated samples (a) $Mn_{54}Al_{42.7}Zn_{3.3}$, (b) $Mn_{54}Al_{44.4}Zn_{1.6}$, (c) $Mn_{53.5}Zn_{0.5}Al_{46}$ in an applied field of 0.05 T and a sweep rate of 5°C/min. Line (d) plots the T-ΔT data from thermal analysis on $Mn_{54}Al_{42.7}Zn_{3.3}$.

4. Conclusions

Zn substitution can stabilize the structure of τ-phase. Zn increases the coercivity and saturation magnetization of the τ-MnAl but reduces the Currie temperature. It should be noted that excess Zn is detrimental to the magnetic

parameters. The optimum magnetic performance was found in samples with Zn substitution to 2.9% Mn atoms and 3.5% Al atoms, respectively.

5. Acknowledgements

6. References

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