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Enhancement of the soft magnetic properties of FeCoZrMoWB bulk metallic glass by microalloying

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Abstract

The $Fe_{61}Co_7Zr_{9.5}Mo_5W_2B_{15.5}$ bulk metallic glass (BMG) has the best glass forming-ability (GFA), high thermal stability, and the highest strength (the compressive strength $\sigma = 3800$ MPa) among known Fe-based alloys. Unfortunately, this BMG does not have the same good soft magnetic properties as other Fe-based BMGs do. We report here that a small amount of Ni addition (microalloying) can significantly enhance the soft magnetic properties of the alloy without deteriorating its high GFA. The saturation magnetization is increased threefold, while the coercivity is decreased about 40-fold, with only 3 at.% Ni addition. The improvement is interpreted to result from the enhancement of the magnetic exchange interaction as the Ni content increases. The results indicate that it is possible to adjust the magnetic properties of Fe-based BMGs by a minor change in the content of some component. BMGs with good soft magnetic property, ultrahigh mechanical strength, good GFA and high thermal stability show some promise for future applications.

The development of soft magnetic metallic glasses with large glass forming ability (GFA) has become an important research topic in recent years because the soft magnetic properties are promising for many applications, such as magnetic conductor and magnetic elements [1–3]. Recently, Fe-based bulk metallic glasses (BMGs) were obtained by a copper mould casting technique at a cooling rate as low as 10^2 K s^{-1} [1]. These BMGs have exceptional GFA, excellent soft magnetic properties (high saturation magnetization M_s and low coercivity, H_c) and high mechanical strength. The alloy with a nominal composition around $Fe_{61}Co_7Zr_{9.5}Mo_5W_2B_{15.5}$ was found to have the by far the best GFA (a maximum diameter of ~6 mm for a rod sample can be obtained), the highest thermal stability (glass transition temperature, $T_g = 898$ K, and crystallization temperature, $T_x = 950$ K), high corrosion

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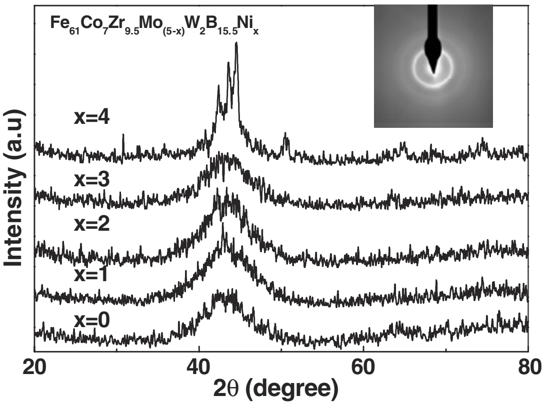

Figure 1. XRD patterns of the as-cast $Fe_{61}Co_7Zr_{9.5}Mo_{5-x}Ni_xW_2B_{15.5}$ (x = 0–4) alloys. The inset displays a selected-area electron diffraction pattern of $Fe_{61}Co_7Zr_{9.5}Mo_5W_2B_{15.5}$ BMG.

resistance and the highest strength (the compressive strength $\sigma = 3800$ MPa, and Vickers hardness $H_v = 1360$) among known Fe-based alloys [4]. Unfortunately, this BMG does not have the same good soft magnetic properties as other Fe-based BMGs [4]. Hence, it is vital to further improve its magnetic properties so that it is more viable for commercialization and future applications.

Recently, minor alloying addition or microalloying technology has already shown dramatic effects on the glass formation of BMGs [4–9]. It has been found that microalloying with proper alloying elements is an effective way to improve the GFA for various BMGs [4–8]. In this paper, we report that the microalloying technology is also very effective for improving the magnetic properties of an Fe-based BMG. Our experimental results demonstrate that a small amount of Ni addition can spectacularly improve the soft magnetic property as well as the electrical behaviour of the $Fe_{61}Co_7Zr_{9.5}Mo_5W_2B_{15.5}$ BMG without markedly deteriorating its high GFA. The role of the Ni addition in the improvement of magnetic properties is discussed.

$Fe_{61}Co_7Zr_{9.5}Mo_{5-x}Ni_xW_2B_{15.5}$ (x = 0–4 at.%) ingots were prepared by arc melting the high purity constituents in a titanium gettered argon atmosphere. Cylindrical samples of these alloys, 2 mm in diameter, were prepared by die casting the remelted ingots into a copper mould under argon atmosphere. The structure of the samples was monitored by x-ray diffraction (XRD) with Cu Kα radiation. The thermal properties associated with the glass transition and crystallization of the alloys were measured using different thermal analysers (DTA; Perkin Elmer DTA7) at a constant heating rate of 10 K min^{-1} under Ar atmosphere. The magnetic properties were measured by a vibrating sample magnetometer (VSM) in an applied field up to 20 000 Oe. The resistance of the specimens was measured by the standard four probe technique using a Physical Properties Measurement System (PPMS6000, Quantum Design Inc. USA) from 1.9 to 300 K. Transmission electron microscopy (TEM) was carried out with a CM200 microscope (Philips Co., The Netherlands) operated at 200 kV accelerating voltage.

The structures of the as-cast $Fe_{61}Co_7Zr_{9.5}Mo_{5-x}Ni_xW_2B_{15.5}$ alloys with x = 0–4 were examined by XRD and shown in figure 1. All these as-cast alloys show a main diffused peak, and no obvious position change of the diffused peak is observed for these samples. The inset displays a selected-area electron diffraction image, which consists of halo rings, indicting the single glassy phase of the as-cast $Fe_{61}Co_7Zr_{9.5}Mo_5W_2B_{15.5}$ alloy. An Ni addition up to 3 at.% does not deteriorate the GFA. However, higher Ni content ($x > 4$) causes the formation of a crystalline phase as shown in figure 1.

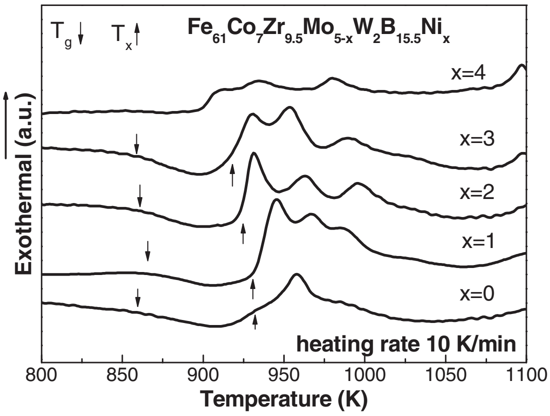

Figure 2. DTA curves of the $Fe_{61}Co_7Zr_{9.5}Mo_{(5-x)}W_2B_{15.5}Ni_x$ (where $x = 0$–4) BMGs. The arrows indicate T_g and T_x.

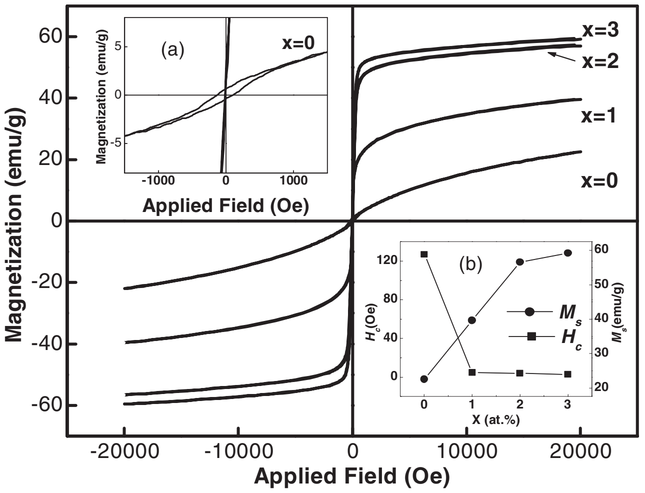

Figure 3. Hysteresis loops measured for the $Fe_{61}Co_7Zr_{9.5}Mo_{5-x}Ni_xW_2B_{15.5}$ ($x = 0$–3) alloys. The inset (a) shows enlarged hysteresis loops. The inset (b) shows the variation of M_s and H_c of the as-cast alloys as a function of Ni addition.

Figure 2 shows DTA scans of the as-cast $Fe_{61}Co_7Zr_{9.5}Mo_{5-x}Ni_xW_2B_{15.5}$ ($x = 0$–4) alloys. When $x < 4$ at.%, the DTA traces exhibit the obvious endothermic characteristic of a glass transition followed by exothermic crystallization reactions at higher temperatures. The crystallization occurs through several exothermic reactions for the alloys with Ni content, but only a single one is observed for the alloy without Ni. However, both T_g and T_x are not markedly changed with the increase of Ni content. The supercooled liquid region, ΔT_x, defined as $T_x - T_g$, is as large as 65–80 K, indicating that the high GFA is retained in the alloys [10]. However, when $x \geqslant 4$, the endothermic peak disappears, and only exothermic peaks of much smaller crystallization enthalpy are observed, implying that the amorphous structure is not the dominating phase in the alloy.

The hysteresis loops of the $Fe_{61}Co_7Zr_{9.5}Mo_{5-x}Ni_xW_2B_{15.5}$ alloys with different Ni contents are displayed in figure 3. The BMG without Ni addition does not show soft magnetic behaviour. The shape of the hysteresis loops (inset (a) shows the enlarged hysteresis loops)

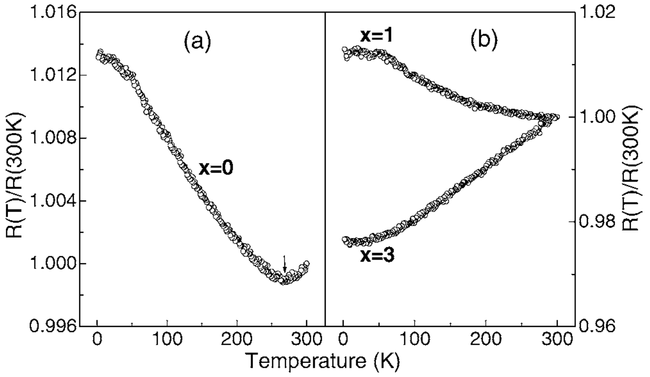

Figure 4. Normalized resistance $R(T)/R(300\text{ K})$ versus temperature. (a) The curve of the $Fe_{61}Co_7Zr_{9.5}Mo_5W_2B_{15.5}$ BMG, (b) the resistance curves of the alloys with 1 and 3 at.% Ni addition. The arrows indicate the position of the minimum.

Table 1. Magnetic properties of the $Fe_{61}Co_7Zr_{9.5}Mo_5W_2B_{15.5}$ alloy prepared and processed under different conditions.

	Sample				
Parameters	As-cast rods	Annealed at 773 K	Annealed at 873 K	As-cast ribbon	3 at.% Ni addition
H_c (Oe)	127.0	36.6	7.3	0	2.97
M_s (emu g^{-1})	22.5	18.1	22.7	16.4	59.1
M_r (emu g^{-1})	0.67	0.98	0.65	0	0.52

for the BMG indicates that it is typical of a magnetic material with large anisotropy field [11]. However, after only 1 at.% Ni addition, the alloy exhibits soft magnetic behaviour. For $x = 2$, and 3, the soft magnetic property of the alloy is much improved. The changes of H_c and M_s as a function of Ni content are shown in the inset (b) of figure 3. H_c decreases rapidly from 127.0 to 4.8 Oe with 1% Ni addition, and then further decreases to 3.0 Oe with increasing the Ni content to 3%. M_s increases from 22.5 to 59.1 emu g^{-1} when the Ni content reach 3%.

Figure 4 shows the normalized resistance $R(T)/R(300\text{ K})$ versus T for the alloys with $x = 0$, 1, and 3. The alloy without Ni addition has a negative temperature coefficient of resistance (TCR) at low temperatures (shown in figure 4(a)), and a resistance minimum occurs at 266 K. The addition of 1% Ni makes the resistance minimum disappear, but the TCR is still negative. The temperature-dependent resistance exhibits substantial changes, and the sign of the TCR turns positive when $x = 3\%$. The marked change of the electric behaviour is mainly associated with the change of magnetic property because no significant changes in structure can be seen from XRD in figure 1 for these alloys. The above results demonstrate that the addition of a small amount of Ni can significantly improve the soft magnetic properties as well as the electrical behaviour of the $Fe_{61}Co_7Zr_{9.5}Mo_5W_2B_{15.5}$ alloy. Such an Fe-based BMG with good GFA, excellent mechanical strength and improved soft magnetic property shows some promise for future applications.

To understand the effect, $Fe_{61}Co_7Zr_{9.5}Mo_5W_2B_{15.5}$ BMG prepared and processed under different conditions was studied, and the results are listed in table 1. Upon annealing around T_g (at 773 and 873 K), H_c decreases markedly while M_s does not change as much as the coercivity. The structural relaxation induced by thermal treatment also greatly changes the magnetic characteristics. Compared to the cast samples, the melt-spun ribbon of the alloy prepared at higher cooling rate exhibits much lower H_c and residual magnetization M_r, which are almost zero in the limit of the measurement device. Compared with BMGs, the ferromagnetic clusters with a certain degree of short-range order in ribbons formed during rapid solidification are smaller [12, 13]. The better soft magnetic properties in the ribbon sample are attributed to the decrease of effective magnetic anisotropy by refining the microstructure. If the cluster size is smaller than the magnetic exchange length, the effective anisotropy decreases, and in turn H_c decreases according to the random anisotropy model [14]. However, the rapid cooling and annealing cannot significantly improve M_s like Ni addition, indicating that Ni addition is more effective in improving the soft magnetic property for a different reason. It is known that Mo is a nonmagnetic metal. However, it has been found that the exchange interaction between Mo and Fe atoms is an 'antiferromagnetic' type based on the observations of the rapid decrease of the Curie temperature of $(Fe_{1-x}Mo_x)_{75}P_{16}B_6Al_3$ alloy with increasing Mo concentration, and the similarity of Mössbauer spectra of $Fe_{80-x}M_xB_{20}$ (M = Cr, Mo) [15, 16]. So, the Ni addition decreases the antiferromagnetic interaction and increases the exchange length, and then leads to the increase of M_s and the decrease of H_c. Another possible reason is that the Ni addition may lower the saturation magnetostriction constant in the alloy, and then this has a contribution to the results.

In conclusion, microalloying with elemental Ni can spectacularly improve the soft magnetic properties of the best BMG-forming and ultrahigh mechanical strength $Fe_{61}Co_7Zr_{9.5}Mo_5W_2B_{15.5}$ alloy without deteriorating its high GFA. The M_s is increased threefold, while the H_c is decreased about 40-fold, with only 3 at.% Ni addition. The improvement is due to the enhancement of the magnetic exchange interaction as the Ni content increases. Our results also indicate that the soft magnetic properties of the Fe-based BMGs can be adjusted by minor changes in the concentration of Ni. The method may be of significance for developing new magnetic BMGs and for understanding the origin of the soft magnetic properties in BMGs.

Acknowledgments

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