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The Large Magnetocaloric Effect in Amorphous $Fe_{80-x}Mn_xZr_{10}$ (x = 4,6,8,10) Alloys

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The Magnetization behaviour has been measured for amorphous $Fe_{90-x}Mn_xZr_{10}$ (x = 4,6,8,10) alloys. The Curie temperature decreased from 236 K to 195 K with increasing Mn concentration (x = 4 to x = 10). The magnetization measurements were conducted at temperatures above the Curie temperature in the paramagnetic region. In all samples, the magnetic properties showed superparamagnetic behavior above T_c where the mean magnetic moment of the superparamagnetic spin clusters decreased with increasing temperature. A large magnetic entropy change, ΔS_M, which is calculated from H vs M curves associated with the ferromagnetic-paramagnetic transitions in amorphous, has been observed. With Mn concentration increasing, ΔS_M decreases 1.04, 0.95, 0.87 J/kg K at 222, 210, 195 K (the Curie temperature), respectively.

Key words : magnetocaloric effect, isothermal magnetization, magnetic refrigeration

1. Introduction

In recent years the materials with high magnetocaloric effect (MCE) have attracted considerable attention as a refrigerant at magnetic refrigeration [1, 2]. Magnetic refrigeration is an environmentally friendly cooling technology and more energy efficiently as compared with vapor-cycle ones. This makes MCE interesting for basic research and investigation meaning possible technological application. MCE is intrinsic to magnetic solids and is induced via the coupling of the magnetic sublattice with the magnetic field, which alters the magnetic part of the total entropy due to a corresponding change of the magnetic field. It can be measured and/or calculated as the adiabatic temperature change $\Delta T_{ad}(T, \Delta H)$, or as the isothermal magnetic entropy change $\Delta S_M(T, \Delta H)$. The MCE is a function of both temperature T and the magnetic field change ΔH and is usually recorded as a function of temperature at a constant ΔH. There is a great deal of interest in exploring new materials with high magnetocaloric effect. As previously [3-8], many rare-earth compounds, especially based on heavy rare-earth elements, may have a high magnetocaloric effect for magnetic refrigeration applications. The calculation of the entropy change by isothermal magnetic measurement is an important way to characterize candidate materials intended for magnetization refrigeration application.

In our work, magnetization and MCE of $Fe_{90-x}Mn_xZr_{10}$ (x = 4,6,8,10) compounds were investigated. These kinds of amorphous materials with low Curie temperature have many useful properties that are attractive for application as magnetic refrigerants.

2. Experiments

Amorphous $Fe_{90-x}Mn_xZr_{10}$ (x = 4, 6, 8, 10) (at %) alloys were prepared by arc melting the high-purity elemental constituents under argon gas atmosphere and by single roller melt spinning in the form of long ribbons of 1~2 mm width and 20~40 μm thickness. The amorphous state of the samples was confirmed through x-ray diffraction studies using Cu-Kα radiation. The magnetization measurements as a function of temperature and field were carried out on a ribbon sample using a vibrating sample magnetometer (VSM) in field up to 10 kOe.

3. Results and Discussion

The nature of the reentrant spin glass transition behavior in Fe-Zr amorphous alloys has been investigated extensively by means of various techniques. The magnetic

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properties of these materials can easily be tuned either by suitable substitutions. While substitution of Mn in place of Fe the magnetic disorder further increases but the system still exhibits reentrant glass behavior. Intense efforts have carried out to understand the nature of the magnetic phase diagram from various magnetic measurements in amorphous Fe-Zr-Mn alloys. The detailed analysis of magnetization data indicated that Mn substitution leads to enhancement of spin fluctuations while application of external magnetic field suppresses the same. The Mn substituted FeZr alloys show some peculiar electrical and magnetic properties. However, it is still debated how and why the magnetic softness increases. It is believed that the enhancement of the soft magnetic properties is due changes in microstructure. We chose a system with higher degree of frustration in order to investigate the reasons for the development of new magnetic caloric materials. According to thermodynamic theory, the magnetic entropy change caused by the variation of the external magnetic field from 0 to H_{max} is given by

$$\Delta S_M = \int_0^{H_{max}} \left(\frac{\partial S}{\partial H}\right)_T dH \tag{1}$$

From Maxwell's thermodynamic relationship

$$\left(\frac{\partial M}{\partial T}\right)_H = \left(\frac{\partial S}{\partial H}\right)_T \tag{2}$$

Equation (1) can be rewritten as follows:

$$\Delta S_M = \int_0^{H_{max}} \left(\frac{\partial M}{\partial T}\right)_H dH \tag{3}$$

Numerical evaluation of the magnetic entropy change was carried out from formula (3) using isothermal magnetization measurements at small discrete field and temperature intervals. ΔS_M can be computed approximately from Eq. (3) by

$$|\Delta S_M| = \sum_i \frac{M_i - M_{i+1}}{T_{i+1} - T_i} \Delta H \tag{4}$$

Figure 1 shows the temperature dependence of low-field magnetization for the samples. The Curie temperature, T_c was found to be 236, 222, 210, 195 K for x = 0, 4, 6, 8 of $Fe_{90-x}Mn_xZr_{10}$, respectively. With an increase of the Mn concentration for $Fe_{90-x}Mn_xZr_{10}$ systems, the Curie temperature decreases almost linearly and then the reentrant behavior is observed in all samples. The magnetization data measured as a function of temperature show that the shape of the magnetization (M) vs. temperature (T) curve is quite sensitive to the applied magnetic field and M decreases as Mn concentration increases. It is

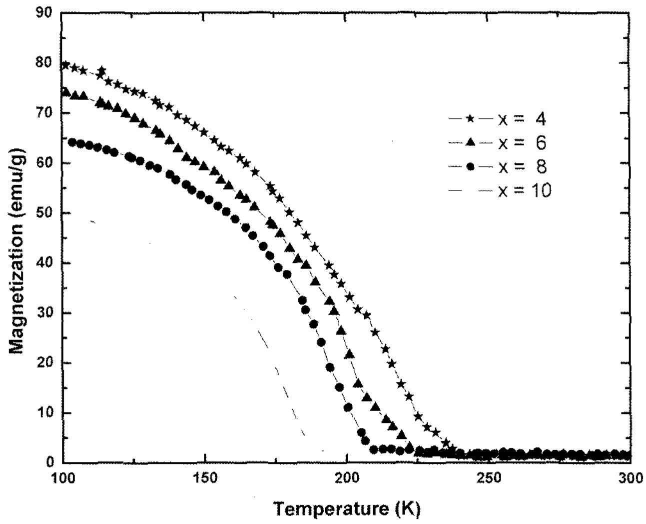

Fig. 1. The magnetization curves in a field of 10 Oe are plotted as a function of temperature for amorphous $Fe_{90-x}Mn_xZr_{10}$, alloys with x = 4, 6, 8, 10.

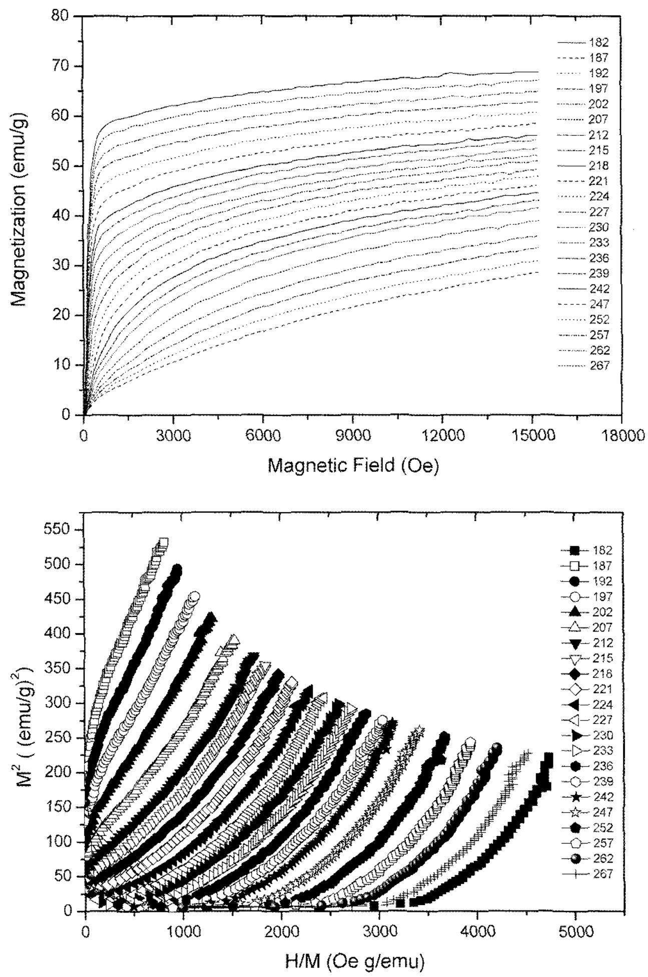

Fig. 2. Isothermal magnetization curves in the vicinity of Curie temperature for $Fe_{86}Mn_4Zr_{10}$ (Top). The H/M vs. M^2 plots for the isotherms of $Fe_{86}Mn_4Zr_{10}$. (Bottom)

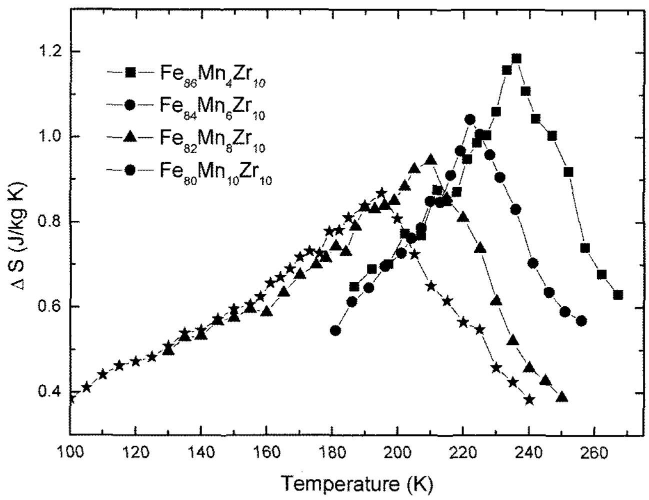

Fig. 3. Temperature dependent magnetic entropy change obtained under a field from 0 to 1.5 T, for x = 4, 6, 8, 10 of $Fe_{90-x}Mn_xZr_{10}$.

believed that the in-homogeneity of amorphous state (frequently referred as clusters) exist in the as-quenched state. Isothermal M-H curves have been measured at various temperatures (see the top panel of Fig. 2). To determine the type of the phase transition for $Fe_{86}Mn_4Zr_{10}$, the measured data for the M-H isotherms were transferred in to H/M vs. M^2 plots and displayed in the bottom panel of Fig. 2. According to mean-field theory, the H/M vs. M^2 isotherms should give a set of straight lines [known as Arrott-Kouvel plots] just below and above T_c [9]. The absence of linear behavior in Fig. 2 suggests that the mean-field theory is not valid for our present case. In evaluating the magnetocaloric properties of the $Fe_{90-x}Mn_xZr_{10}$, (x = 4, 6, 8, 10) samples, the magnetic entropy change as a function of temperature and magnetic field, produced by the variation of the magnetic field from 0 to H_{max} is calculated by Eq. (4). Temperature dependence of magnetic entropy change, ΔS_M, was plotted in Fig. 3. As can be seen in Fig. 3 with a magnetic field varying from 0 to 1.5 T, the magnetic entropy change ΔS_M reaches a maximum value of about 1.19 J/kg K for x=4 at 236 K. With Mn concentration increasing, ΔS_M decreases 1.04, 0.95, 0.87 J/kg K at 222, 210, 195 K (the Curie temperature), respectively.

In conclusion, the magnetic properties and entropy changes of Fe-Mn-Zr amorphous alloys were investigated. The Curie temperature decreases with increasing Mn concentration, and the peaks of entropy change appear at the Curie temperature region. The entropy changes decreases with increasing Mn concentration. In comparison with Gd metal, the peaks are broader around the Curie temperature. Our results indicate that these ribbon samples are very useful for wideband temperature materials.

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