Article

Effect of Co/Ni Substituting Fe on Magnetocaloric Properties of Fe-Based Bulk Metallic Glasses

Jia Guo ^{1,2}, Lei Xie ^{1,2}, Cong Liu ³, Qiang Li ^{1,2,*} , Juntao Huo ^{4,*}, Chuntao Chang ⁵, Hongxiang Li ⁶ and Xu Ma ^{1,2}

¹ Xinjiang Key Laboratory of Solid State Physics and Devices, Xinjiang University, Urumqi 830046, China; 1437439380@stu.xju.edu.cn (J.G.); guo15276862660@163.com (L.X.); 15299660877@163.com (X.M.)

² School of Physics Science and Technology, Xinjiang University, Urumqi 830046, China

³ School of Materials Science and Engineering, Tianjin University, Tianjin 300072, China; liucong010243@163.com

⁴ Key Laboratory of Magnetic Materials and Devices, Ningbo Institute of Materials Technology & Engineering, Chinese Academy of Sciences, Ningbo 315201, China

⁵ School of Mechanical Engineering, Dongguan University of Technology, Dongguan 523808, China; changct@dgtu.edu.cn

⁶ State Key Laboratory for Advanced Metals and Materials, University of Science and Technology Beijing, Beijing 100083, China; hxli@skl.ustb.edu.cn

* Correspondence: qli@xju.edu.cn (Q.L.); huojuntao@nimte.ac.cn (J.H.)

Abstract: In this work, $\text{Fe}_{80-x}\text{M}_x\text{P}_{13}\text{C}_7$ ($\text{M} = \text{Co}, \text{Ni}; x = 0, 5 \text{ and } 10 \text{ at.}\%$) bulk metallic glasses (BMGs) were prepared, and the effect of the Co/Ni elements substitution for Fe on the magnetocaloric properties of $\text{Fe}_{80}\text{P}_{13}\text{C}_7$ BMG has been investigated systematically. The Curie temperature (T_C) of the present Fe-based BMGs increases with the substitution of Fe by Co/Ni. The magnetic entropy change (ΔS_M) of the present Fe-based BMGs increases first and then decreases with the increase of Fe substituted by Co, but monotonically decreases with the increase of Fe substituted by Ni. Among the present Fe-based BMGs, the $\text{Fe}_{75}\text{Co}_5\text{P}_{13}\text{C}_7$ BMG exhibits the maximum ΔS_M value of $5.21 \text{ J kg}^{-1} \text{ K}^{-1}$ at an applied field of 5 T, which is the largest value among Fe-based amorphous alloys without any rare earth elements reported so far. The present Fe-based BMGs exhibit the large glass forming ability, tunable T_C and enhanced ΔS_M value, which are beneficial for magnetic refrigerant materials.

Keywords: Fe-based bulk metallic glasses; Co/Ni substitution for Fe; magnetocaloric effect

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1. Introduction

Compared with the traditional refrigeration technology of compressed gas medium, the magnetic refrigeration technology [1,2] is an environmentally friendly technology with high efficiency, low energy consumption and no environmental pollution [3,4]. Up to now, a series of the crystalline compounds, for example, Gd-Si-Ge [5,6], La-Fe-Si [7] and Mn-Fe-P-Ps [8], etc., show a giant magnetic entropy change (ΔS_M) based on the first order magnetic phase transition (FOMT), but also some shortcomings including the low corrosion resistance, high hysteresis losses and expensive raw materials, which greatly limit the application of these materials in the field of magnetic refrigeration [9,10]. Compared with the FOMT magnetocaloric materials, metallic glasses, e.g., Fe-based amorphous alloys, exhibit magnetocaloric effects based on the second order magnetic phase transition (SOMT) and possess the unique advantages of magnetic refrigeration materials, such as superior mechanical properties, low hysteresis and thermal hysteresis, higher electrical resistivity, and so on [11,12]. Moreover, Fe-based amorphous alloys show great potential for commercial use because of their abundant raw materials. However, Fe-based amorphous alloys show a low value of ΔS_M frequently, which greatly restricts their application as magnetic refrigeration materials [13]. Therefore, it is of significance and importance for Fe-based amorphous alloys to improve magnetocaloric properties.

Many studies have indicated that the element addition to Fe-based amorphous alloys may cause significant changes in their magnetocaloric properties. Usually, the rare earth elements are chosen to be a regulating element and are added into Fe-based amorphous alloys to improve magnetocaloric properties due to their large atomic magnetic moments. Recent studies show that minor additions of Gd or Dy elements increase the value of ΔS_M while the excessive addition of Gd or Dy causes the value of ΔS_M to decrease [14]. However, Ce element addition leads to the decrease of ΔS_M [15] in Fe-Si-Nb-B-Cu metallic glasses. The addition of transition metals usually increases the T_C and ΔS_M of Fe-based amorphous alloys due to the stronger atomic exchange interaction. The addition of Cu improves the magnetocaloric properties of Fe-Zr amorphous alloys [16]. The partial substitution of Fe by Co and Ni in Fe-Zr-B-Cu amorphous alloy leads to the increase of T_C , and appropriate doping Co and Ni elements enhances the value of ΔS_M for $\text{Fe}_{71.5}\text{Co}_{8.25}\text{Ni}_{8.25}\text{Zr}_7\text{B}_4\text{Cu}_1$ amorphous alloy [17]. These results indicate that systematic investigation of the effect of transition metals on magnetocaloric effect should be significant.

Previous studies showed that $\text{Fe}_{80}\text{P}_{13}\text{C}_7$ bulk metallic glass (BMG) exhibited excellent magnetocaloric performance with the ΔS_M of $5.05 \text{ J kg}^{-1} \text{ K}^{-1}$ under an applied field of 5 T [18]. To further increase the ΔS_M value of $\text{Fe}_{80}\text{P}_{13}\text{C}_7$ BMG, the glass forming ability (GFA), magnetic properties and magnetocaloric performance of $\text{Fe}_{80}\text{P}_{13}\text{C}_7$ BMG affected by partially substituting the transition metals (Co/Ni) for Fe were investigated systematically.

2. Experiment

$\text{Fe}_{80-x}\text{M}_x\text{P}_{13}\text{C}_7$ (M = Co, Ni; x = 0, 5 and 10 at.%) alloy ingots were prepared by torchmelting the high purity elements Fe powders (99.9% pure), Fe_3P Powders (99.5% pure), graphite powders (99.9% pure), cobalt powders (99.9% pure) and nickel powders (99.7% pure) with a torch in a clean quartz tube under a high-purity argon atmosphere. The ingots were then placed into clean quartz tubes containing a fluxing agent of B_2O_3 and CaO powder (mass ratio = 3:1) and fluxed in a vacuum at 1150 degrees for 4 h. After that, the glass alloy rods with a maximum diameter of 2.5 mm and a length of several centimeters were produced by the J-quenching technique [18].

The structure of the alloy rods was measured by Bruker D8 advance X-ray diffractometer (XRD) (Bruker, Billerica, MA, USA) with Cu K α radiation. The rod samples were smashed to small pieces by a hammer before the XRD test to obtain the pattern with good quality. The thermal behavior of the glassy rod was estimated by NETZSCH DSC 404F1 differential scanning calorimetry (DSC) (NETZSCH, Selb, Germany) with a heating rate of 0.33 K/s under an Ar atmosphere. The magnetic hysteresis loop of glassy rod samples was tested with the maximum applied field up to 10,000 Oe at the room temperature by a Lake Shore 7400 vibrating sample magnetometer (VSM) (Lake Shore, Carson, CA, USA). The field and temperature dependences of magnetization curves of the glassy rods were tested by Quantum Design[®] superconducting quantum interference device magnetometer (MPMS) (Quantum Design Int., San Diego, CA, USA), in which the measurement specimens were first cut about 3 mm from the bulk glassy rods with a diameter of 1 mm and then ground into rectangular slices with around 40 μm thick and 1 mm width. The temperature interval is 10 K away from T_C and 5 K near the T_C in the isothermal magnetization curve measurements. The density of the samples was determined by Archimedes' method. Except for XRD test, the samples used in other tests are all 1 mm in diameter to avoid the risk of partial crystallization.

3. Result and Discussion

The XRD patterns of the as-cast $\text{Fe}_{80-x}\text{M}_x\text{P}_{13}\text{C}_7$ (M = Co, Ni; x = 0, 5 and 10 at.%) alloy rods with the corresponding maximum diameters (D_{max}) for fully glass formation [19,20] are shown in Figure 1. There are only typical halo peaks and no crystalline peaks in the XRD patterns of all the samples, verifying the fully glassy phase formation. Figure 2 shows the DSC curves of the as-cast glassy alloy rod specimen. All the curves show the sequential transition of the glass transition, supercooled liquid region and two-step crystallization.

The DSC curves can further confirm the glassy structure of the present samples. With the substitution content of both Co and Ni for Fe increases from 0 to 10 at.%, the D_{max} of the present Fe-based BMGs increases from 2.0 to 2.5 mm, indicating that substituting Fe with a minor amount of Co/Ni can increase the GFA of $\text{Fe}_{80}\text{P}_{13}\text{C}_7$ alloy to a certain extent.

Figure 1. XRD patterns of the as-cast $\text{Fe}_{80-x}\text{M}_x\text{P}_{13}\text{C}_7$ ($\text{M} = \text{Co}, \text{Ni}$; $x = 0, 5$ and 10 at.%) alloy rods with the corresponding maximum diameter for fully glass formation.

Figure 2. DSC curves of the as-cast $\text{Fe}_{80-x}\text{M}_x\text{P}_{13}\text{C}_7$ ($\text{M} = \text{Co}, \text{Ni}$; $x = 0, 5$ and 10 at.%) glassy alloy rods at a heating rate of 0.33 K/s.

Figure 3 shows the hysteresis loops of the as-cast $\text{Fe}_{80-x}\text{M}_x\text{P}_{13}\text{C}_7$ ($\text{M} = \text{Co}, \text{Ni}; x = 0, 5$ and 10 at.%) glassy rods tested by VSM, and the determined saturation magnetization (J_s) of the measured samples are shown in Table 1. All the glassy rod samples show good soft magnetic performance and low coercivity. The J_s of the glassy rod samples firstly increases from 160 to 165 emu/g with the increase of Co substituting for Fe from 0 to 5 at.%, and then decreases to 157 emu/g when the Co content reaches 10 at.%, while the J_s value monotonically decreases from 160 to 150 emu/g with the Ni substitution for Fe increases from 0 to 10 at.%.

Figure 3. The hysteresis loops of the as-cast $\text{Fe}_{80-x}\text{M}_x\text{P}_{13}\text{C}_7$ ($\text{M} = \text{Co}, \text{Ni}; x = 0, 5$ and 10 at.%) glassy alloy rods at room temperature and the inset is the enlarged part of the magnetization curve.

Table 1. The maximum diameter for fully glass formation (D_{max}), magnetic transition temperature (T_C), the saturation magnetization (J_s) and magnetocaloric properties at the magnetic applied field of 1.5 T and 5 T for the present $\text{Fe}_{80-x}\text{M}_x\text{P}_{13}\text{C}_7$ ($\text{M} = \text{Co}, \text{Ni}; x = 0, 5$ and 10 at.%) BMGs.

Composition (at.%)	D_{max} (mm)	T_C (K)	J_s (emu/g)	$-\Delta S_M$ (J kg ⁻¹ K ⁻¹)		ΔT_{FWHM} (K)		RC_{FWHM} (J kg ⁻¹)	
				1.5 T	5 T	1.5 T	1.5 T	5 T	5 T
$\text{Fe}_{80}\text{P}_{13}\text{C}_7$	2.0	581	160	2.20	5.05	57.1	125.6		479.8
$\text{Fe}_{75}\text{Co}_5\text{P}_{13}\text{C}_7$	2.3	623	165	2.34	5.21	39.1	91.6		331.6
$\text{Fe}_{70}\text{Co}_{10}\text{P}_{13}\text{C}_7$	2.5	649	157	2.08	4.98	55.4	115.2		462.1
$\text{Fe}_{75}\text{Ni}_5\text{P}_{13}\text{C}_7$	2.5	596	155	2.04	4.60	52.2	106.5		381.8
$\text{Fe}_{70}\text{Ni}_{10}\text{P}_{13}\text{C}_7$	2.5	600	150	1.46	3.26	48.7	71.1		211.2

Figure 4a shows that the temperature varies with magnetization (M - T curve) of the as-cast $\text{Fe}_{80-x}\text{M}_x\text{P}_{13}\text{C}_7$ ($\text{M} = \text{Co}, \text{Ni}; x = 0, 5$ and 10 at.%) glassy rod samples tested by MPMS at a magnetic applied field of 0.02 T, and Figure 4b shows the T_C determined by the differentiation of M - T curves and summarized in Table 1. It can be concluded that with the increase of Co/Ni substituting Fe, the T_C of Fe-based BMGs increases, and further the rise rate of T_C with the Co content is greater than that with the Ni content. Based on the mean field theory, T_C is proportionate to the saturation magnetization and the exchange integral, in which the exchange integral is dependent on the distance between magnetic atoms [21]. The radii of Fe, Co and Ni atoms are 0.124 nm, 0.125 nm and 0.125 nm, respectively [22]. Therefore, based on the Bathe-Slater curve [21], the replacement of Co/Ni for part of Fe caused a stronger atomic exchange interaction, and thus the higher T_C .

Figure 4. Temperature varies with magnetization (a) and dM/dT (b) of as-cast Fe_{80-x}M_xP₁₃C₇ (M = Co, Ni; x = 0, 5 and 10 at.%) glassy alloy rod samples.

The isothermal magnetization curves of the Fe_{80-x}M_xP₁₃C₇ (M = Co, Ni; x = 0, 5 and 10 at.%) glassy alloy rod samples at the magnetic applied fields of 1.5 to 5 T are shown in Figure 5. When the test temperature is below T_C , the samples reach the magnetization saturation under low applied magnetic fields, but when the temperature gets close to or above T_C , the M - H curves of the samples become linear, indicating that the samples turn from ferromagnetic to paramagnetic state [23].

Figure 5. The isothermal magnetization curves of $\text{Fe}_{80-x}\text{M}_x\text{P}_{13}\text{C}_7$ ($\text{M} = \text{Co}, \text{Ni}$; $x = 0, 5$ and 10 at.%) glassy alloy rods at the magnetic applied fields up to 5 T.

In most research on characterization of magnetocaloric materials, the magnetic entropy change (ΔS_M) is an important parameter and ΔS_M under the applied maximum magnetic field of H_{max} is defined as the follow equation [3,24]:

$$\Delta S_M = \int_0^{H_{max}} \left(\frac{\partial M}{\partial T} \right)_H dH \quad (1)$$

where M is the magnetization under the applied magnetic field of H . Equation (1) can also be written in other terms:

$$\Delta S_M (T_i, H_{max}) = \frac{\int_0^{H_{max}} M(T_i, H) dH - \int_0^{H_{max}} M(T_{i+1}, H) dH}{T_i - T_{i+1}} \quad (2)$$

where $M(T_i, H)$ and $M(T_{i+1}, H)$ are the magnetization at the temperature of T_i and T_{i+1} , respectively, and under the applied magnetic field of H . Based on the M - H curves of the samples at different temperature in Figure 6, the change of $-\Delta S_M$ with temperature of $\text{Fe}_{80-x}\text{M}_x\text{P}_{13}\text{C}_7$ ($\text{M} = \text{Co}, \text{Ni}$; $x = 0, 5$ and 10 at.%) glassy rod samples under the different applied maximum fields can be constructed according to Formula (2) and is shown in

Figure 6, and the peak values ($|\Delta S_M^{\text{peak}}|$) determined from the $\Delta S_M - T$ curve of the samples under the applied field of 1.5 T and 5.0 T are summarized in Table 1. The $|\Delta S_M^{\text{peak}}|$ values of $\text{Fe}_{80}\text{P}_{13}\text{C}_7$, $\text{Fe}_{75}\text{Co}_5\text{P}_{13}\text{C}_7$, $\text{Fe}_{70}\text{Co}_{10}\text{P}_{13}\text{C}_7$, $\text{Fe}_{75}\text{Ni}_5\text{P}_{13}\text{C}_7$ and $\text{Fe}_{70}\text{Ni}_{10}\text{P}_{13}\text{C}_7$ are 2.20, 2.34, 2.08, 2.04 and 1.46 $\text{J kg}^{-1} \text{K}^{-1}$ at an applied field of 1.5 T, respectively, and 5.05, 5.21, 4.98, 4.60 and 3.26 $\text{J kg}^{-1} \text{K}^{-1}$ at an applied field of 5.0 T, respectively. Compared to the $\text{Fe}_{80}\text{P}_{13}\text{C}_7$ BMG, replacing 5 at.% of Fe by Co increases the value of $|\Delta S_M^{\text{peak}}|$ while 10 at.% substitution of Co for Fe reduces the value of $|\Delta S_M^{\text{peak}}|$; the value of $|\Delta S_M^{\text{peak}}|$ continuously decreases with the increasing of Ni substituted for Fe content. It can be found that the changing trend of $|\Delta S_M^{\text{peak}}|$ value is consistent with that of J_s value with the substitution of Co/Ni for Fe in the present Fe-based BMGs. Many studies [24] have pointed out that there is a positive correlation between the J_s of magnetic materials and the $|\Delta S_M^{\text{peak}}|$. The $|\Delta S_M^{\text{peak}}|$ as a function of J_s for the present $\text{Fe}_{80-x}\text{M}_x\text{P}_{13}\text{C}_7$ ($\text{M} = \text{Co}, \text{Ni}; x = 0, 5$ and 10 at.%) BMGs at the magnetic applied field of 1.5 T and 5.0 T are shown in Figure 7, in which the good linear relationship with the R-square value of 0.864, indicates that the present Fe-based BMGs follow this correlation relationship.

Figure 6. Magnetic entropy changes as a function of temperature under 1.5–5 T for $\text{Fe}_{80-x}\text{M}_x\text{P}_{13}\text{C}_7$ ($\text{M} = \text{Co}, \text{Ni}; x = 0, 5$ and 10 at.%) glassy alloy rods.

Figure 7. The relationship between saturation magnetization (J_s) at room temperature and the maximum magnetic entropy changes ($|\Delta S_M^{\text{peak}}|$) of $\text{Fe}_{80-x}\text{M}_x\text{P}_{13}\text{C}_7$ ($\text{M} = \text{Co}, \text{Ni}$; $x = 0, 5$ and 10 at.%) glassy alloy rods at a magnetic applied field of 1.5 T.

Another important parameter that is often applied for the characterization of magnetocaloric effect is refrigeration capacity (RC), which equals to the area of the $\Delta S_M - T$ curve. The RC_{FWHM} can be obtained by the following equation [17,25]:

$$RC_{FWHM} = -\Delta S_M^{\text{peak}} \times \Delta T_{FWHM} \quad (3)$$

where ΔT_{FWHM} is the temperature interval corresponding to the half-width of the $\Delta S_M - T$ curve. The ΔT_{FWHM} and RC_{FWHM} values of each glassy rod samples are listed in Table 1. We can see that the RC_{FWHM} of the $\text{Fe}_{80}\text{P}_{13}\text{C}_7$, $\text{Fe}_{75}\text{Co}_5\text{P}_{13}\text{C}_7$, $\text{Fe}_{70}\text{Co}_{10}\text{P}_{13}\text{C}_7$, $\text{Fe}_{75}\text{Ni}_5\text{P}_{13}\text{C}_7$, $\text{Fe}_{70}\text{Ni}_{10}\text{P}_{13}\text{C}_7$ glassy rods are 125.6 , 91.6 , 115.2 , 106.5 , 71.1 J kg^{-1} under 1.5 T, respectively. It is worth noting that, compared with the $\text{Fe}_{80}\text{P}_{13}\text{C}_7$ BMG, the $\text{Fe}_{80-x}\text{Co}_x\text{P}_{13}\text{C}_7$ BMG shows the larger $|\Delta S_M^{\text{peak}}|$ but smaller RC_{FWHM} , which is attributed to the smaller ΔT_{FWHM} of the $\text{Fe}_{75}\text{Co}_5\text{P}_{13}\text{C}_7$ BMG, as shown in Table 1. The smaller ΔT_{FWHM} is presumably the stronger magnetic coupling in the $\text{Fe}_{75}\text{Co}_5\text{P}_{13}\text{C}_7$ BMG.

4. Conclusions

In this work, the $\text{Fe}_{80-x}\text{M}_x\text{P}_{13}\text{C}_7$ ($\text{M} = \text{Co}, \text{Ni}$; $x = 0, 5$ and 10 at.%) bulk glassy rods are fabricated by combining fluxing treatment and the J-quenching technique. Moreover, their magnetocaloric properties are investigated. The replacement of Co/Ni for Fe caused the increase of T_C from 579 K for $x = 0$ to 649 K for $\text{M} = \text{Co}$, $x = 10$ and 600 K for $\text{M} = \text{Ni}$, $x = 10$. The $|\Delta S_M^{\text{peak}}|$ and RC_{FWHM} values of $\text{Fe}_{80}\text{P}_{13}\text{C}_7$, $\text{Fe}_{75}\text{Co}_5\text{P}_{13}\text{C}_7$, $\text{Fe}_{70}\text{Co}_{10}\text{P}_{13}\text{C}_7$, $\text{Fe}_{75}\text{Ni}_5\text{P}_{13}\text{C}_7$, $\text{Fe}_{70}\text{Ni}_{10}\text{P}_{13}\text{C}_7$ are 5.05 , 5.21 , 4.98 , 4.60 , 3.26 $\text{J kg}^{-1} \text{K}^{-1}$, and 479.8 , 331.6 , 462.1 , 381.8 , 211.2 J kg^{-1} , respectively, at the magnetic applied field of 5 T. Significantly, the $\text{Fe}_{75}\text{Co}_5\text{P}_{13}\text{C}_7$ amorphous alloy exhibits the largest value of $|\Delta S_M^{\text{peak}}|$ in the Fe-based amorphous alloys without any rare earth elements as reported so far. The high T_C of the present BMGs may limit their application but can be lowered to room temperature by adding some selected elements, which makes them possible for room temperature magnetic refrigeration.

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