The existence of large magnetocaloric effect at low field variation and the anti-corrosion ability of Fe-rich alloy with Cr substituted for Fe

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Abstract. The influence of Cr substituted for Fe in Fe\textsubscript{78-x}Cr\textsubscript{x}Si\textsubscript{4}Nb\textsubscript{5}B\textsubscript{12}Ag\textsubscript{1} ribbons on the crystallization and magnetic properties including the magnetocaloric effect have been investigated. DSC measurements showed that the crystallization temperature and the crystallization activation energy increased with Cr content. Thermomagnetic curves measured in low applied field indicated that there is a sharp ferromagnetic-paramagnetic phase transition at Curie temperature, \(T_C\), of the amorphous phase. In addition, substitution of Cr for Fe led to approximate linear decrease of \(T_C\) with Cr content, namely from 450K to 280K for \(x = 0\) and \(x = 8\), respectively. From a series of the isothermal magnetization curves \(M(H)\) measured at different temperatures, magnetic entropy change \(\Delta S_m\) was determined at magnetic field variations of 13.5, 10.0 and 5.0 kOe. Maximum value of \(\Delta S_m\) (occurred near \(T_C\)) decreased with increasing Cr content and these values established are quite large at low field variation. Namely, at moderate low magnetic field variation of 5.0 kOe, \(\Delta S_{m_{\text{max}}}\) is of 4.4 and 1.9 J/kg.K for \(x = 0\) and \(x = 8\), respectively. Our studied alloys system could be considered as the best magnetocaloric material candidates for magnetic refrigeration because of colossal magnetic entropy change at low field variation and working temperature could be controlled in large region by substitution effect. The anti-corrosion ability of alloys was also examined.

Keywords: Magnetocaloric effect, anti-corrosion, amorphous ribbons.

1. Introduction

Magnetic refrigeration recently is a current topic in solid state physics/materials science and is of interest to physicists, materials scientists, and electrical and/or electric engineers. Magnetic cooling using magnetocaloric effect (MCE) has much interest of commercial applications in magnetic refrigeration as well as of fundamental research. Magnetic refrigeration using solid substances offers a lot of advantages over conventional gas compression refrigeration, namely:

(i) high thermodynamic efficiency due to reversibility of the MCE (e.g. the efficiency of magnetic refrigeration can be reached up to 60% of a Carnot cycle, whereas the efficiency is only 5–10% for conventional vapour compression refrigeration),

(ii) high energy densities and more compact devices because the working medium is a solid rather than a gas,

(iii) natural recovery of magnetic work during the cycle,
usage of common liquids as heat transfer fluids (e.g. water, water-alcohol solution, air, or helium gas) with no ozone - depleting and/or global - warning effects, lower cost as using inexpensive magnet systems (e.g. permanent magnets), environmental protection because it eliminate the chlorofluoro-carbons present in high-temperature gas-cycle systems.

Magnetic refrigeration has many potential applications in energy intensive industrial and commercial refrigerator systems, such as large–scale air conditioners, heat pumps, supermarket refrigeration units, waste separation, chemical processing, gas liquefaction, liquor distilling, sugar refining, grain drying etc... MCE, or adiabatic temperature change which is detected as the heating or cooling of magnetic materials due to a varying magnetic field, was originally discovered in iron by Warburg [1]. When an external magnetic field is applied to a material, the magnetic spins in the material attempt to align with the magnetic field, thereby reducing the magnetic entropy of the spin system. If this process is performed adiabatically, the reduction of the spin entropy is offset by an increase in lattice entropy, and the temperature of the sample will rise. If the magnetic field is subsequently removed, the temperature of sample will reduce. This warming and cooling is response to the application and removal of an external magnetic field is called MCE. Therefore the MCE is intrinsic to all magnetic materials.

As we well know, the magnetic entropy change, \( \Delta S_m \), and the adiabatic temperature change, \( \Delta T_{ad} \), are correlated with the magnetization, the magnetic field strength, the heat capacity and the working temperature by the fundamental Maxwell’s relations [2]:

\[
\Delta S_m (T, H) = \int_0^{H_{max}} \frac{\partial M(T, H)}{\partial T} \, dH ,
\]

and

\[
\Delta T_{ad} (T, \Delta H) = - \int_0^{H_{max}} \frac{T}{C(T, H)} \left( \frac{\partial M(T, H)}{\partial T} \right)_H \, dH ,
\]

where \( H_{max} \) is the final applied magnetic field. Equations (1) and (2) have a fundamental importance on the understanding of the behaviour of the MCE in solid and serve as a guide for the search of new materials with a large MCE [3]. Conventional magnetic refrigerants fall into two categories: first, the paramagnetic salts used to obtain mK, and second, ferromagnetic materials working in the vicinity of their ordering temperature. Recently, there has been particular interest in extending the magnetic refrigeration technique to room temperature region because of the desire to eliminate the chlorofluoro-carbons presented in high-temperature gas-cycle systems (environmental concerns) as well as potential impact of energy savings. Therefore materials with large MCE are needed to improve energy efficiency.

The prototype material for the room temperature range is the lanthanide metal Gd which orders ferromagnetically at 294K. Its MCE has been studied independently by many authors and the \( \Delta T_{ad} \) values at \( T_c \) are 6, 12, 16 and 20K for \( \Delta H = 2, 5, 7.5 \) and 10 T, respectively (see, for example [4]). A series of \( \text{Gd}_a(\text{Si},\text{Ge}_{1-a})_4 \) alloys was reported [5, 6] to display MCE at least two times larger than that of Gd near room temperature and between 2 to 10 times larger than that of the best (at that time) magnetocaloric materials in the low and intermediate temperature regions. Many other materials have been studied with respect to their magnetocaloric properties [7]. The compounds \( \text{La(Fe,Si)}_{13} \) and \( \text{La(Fe,Al)}_{13} \) [8], \( \text{MnFeP}_{1-x}\text{As}_x \) [9], \( \text{MnAs}_{1-x}\text{Sb}_x \) [10] are suggested to be the potential candidates for room temperature magnetic refrigerators. Another class of materials also displaying the large MCE (comparable to Gd) is based on perovskite [11-15]. Especially, for the first time we are examined the positive magnetic entropy change in manganite with charge-ordering [16].

Recently, the research group at Center for Materials of Science, Vietnam National University, Hanoi have examined the influence of P substituted for B [17], Ag, Zn and Au for Cu [18-20], Co, Mn, Cr and Nb for Fe [21-24] in Finemet on the crystallization and properties of materials. We have
discovered giant magnetocaloric effect in a series of amorphous alloys typical Finemet (Fe$_{73.5}$Si$_{13.5}$B$_{9}$Nb$_{3}$Cu$_{1}$) and like-Finemet [25, 26]. The maximum magnetic entropy change reached quite large value comparing within world studies. Namely, this value is of 13.9 J/kg.K, 11.2 J/kg.K in reference [25] and 9.8 J/kg.K in reference [27] at moderate low field change (1.35 T) and occurs at a temperature that is higher than room temperature. Also, the working temperature can be easily controlled by substitution effect. However, this temperature is rather high and the value of magnetic entropy change strongly decreases when T$_C$ reaches around room temperature.

In this report, we present the results of large MCE at a low field variation and anti-corrosion ability in Fe-rich alloys: Fe$_{78-x}$Cr$_x$Si$_4$Nb$_5$B$_{12}$Ag$_1$.

2. Experimental

The soft magnetic ribbons Fe$_{78-x}$Cr$_x$Si$_4$Nb$_5$B$_{12}$Ag$_1$ (x = 0 - 8) have been prepared by rapid quenching technique on a single copper wheel. The linear speed of the wheel for all ribbons was 30 m/s. The structure of the samples was examined by X-ray diffractometer D5005 Bruker. The thermal transition analysis was studied by a differential scanning calorimeter SDT 2960 TA Instruments. The ribbons were annealed in vacuum. The thermomagnetic curves of as-cast ribbons were measured by vibrating sample magnetometer (VSM) DMS 880 Digital Measurement System and the magnetic properties of studied samples were determined by using Permagraph AMH-401 A, Walker. In order to examine the chemical anti-corrosion, we chose the samples with different Cr content having the same thickness and width (the same area). These samples are soaked in a solution of diluted brine (concentration c = 5‰) and after 4 days, they are drawn out and dried. The mass depression is determined by the balance whose accuracy is 10$^{-5}$ g.

3. Results and discussion

The XRD patterns of as-cast samples showed one broad peak centered at approximately 2$\theta$ = 45° which appears to be typical for an amorphous phase.

![Figure 1.](image1.png)  
**Figure 1.** DSC curves of as-cast ribbon with x = 0 measured with heating rate from 10 to 50°C/min.

DSC measurement on as-cast amorphous ribbons was performed with heating rate from 10 to 50°C/min in Ar atmosphere. Figure 1 shows DSC curves for the sample with x = 0 as an example. There are three separated exothermal peaks T$_{p1}$, T$_{p2}$ and T$_{p3}$ on DSC curves. The first peak corresponds the formation of $\alpha$-Fe(Si) phase and partial FeCr phase (T$_{p1}$). On a crystallographic level, $\alpha$-Fe(Si) and FeCr phases are the same structure of bcc, so on the XRD patterns and DSC curves, three phases are close. Because of the resolution of device is not high, the phase splitting is not observed. The second and third peaks on DSC curves ascribe to the precipitation of boride phases (T$_{p2}$ and T$_{p3}$) depending on the Cr content substituted for Fe.

![Figure 2.](image2.png)  
**Figure 2.** Kissinger plot for determination of crystallization activation energy of the first peak for the sample with x = 0.

$$E_a = 2.03 \text{ eV}$$
Based on DSC patterns measured at different heating rates and Kissinger plots (figures 1 and 2), we have evaluated the crystallization activation energy \( E_{a1} \) of the first peak [28]. The formation of FeCr phase with laminar structure [27] makes the exothermal peaks (\( T_{p1} \), \( T_{p2} \) and \( T_{p3} \)) and the crystallization activation energy increase with the Cr content due to the laminar structure have the shape magnetic anisotropy.

For the first time, Leu and Chin [29] have pointed out the use of DTA apparatus for estimating the crystallization volume fraction. The as-cast ribbons have been annealed from 505 to 545°C (depending on Cr content) for 90 minutes. Using Leu and Chin expression, we derive the crystallization volume fraction of the \( \alpha \)-Fe(Si) phase and the results indicate to be 82%.

From the X-ray analysis, we can determine the average grain size of \( \alpha \)-Fe(Si) particles formed after annealing according to the Sherrer expression [30] and the lattice constant using Bragg’s diffraction. The results are shown in figure 3 and table 1. The grain size decreases while the lattice constant slightly increases with increasing Cr content. There is due to that the higher Cr content, the higher crystallization activation energy that leads to hard crystallization. Moreover, the radius of Fe ion is less than that of Cr ion, therefore the higher Cr content leads to the lattice deformation and make increasing the lattice constant. We know that the grain size and the crystallization phase depend on the annealing regime (annealing temperature and keeping time). The grain size depends majorly on annealing temperature, so the samples with higher Cr content annealed at the higher temperature, and the average grain size increases.

Because of nanosize and appropriate volume fraction of \( \alpha \)-Fe(Si) phase, the soft magnetic properties of annealed sample have been remarkably improved compared to those of as-cast samples (figure 4 and table 1). However, the soft magnetic properties of the sample with \( x = 7 \) is worse than those of the sample with \( x = 0 \) due to ferromagnetic dilution and the formation of FeCr phase.

| Sample | \( T_{p1} \) (°C) | \( E_{a1} \) (eV) | \( a \) (nm) | \( D \) (nm) | \( H_C \) (Oe) | \( \mu_{\text{max}} \) |
|--------|-----------------|-----------------|-------------|-------------|---------------|---------------|
|        |                 |                 |             |             | as-spun       | annealed      |
| \( x = 0 \) | 528            | 2.03            | 0.2941      | 25.1        | 0.13          | 0.01          |
| \( x = 7 \) | 580            | 2.70            | 0.2963      | 20.7        | 0.25          | 0.08          |

**Table 1.** Several characteristics of the ribbons with \( x = 0 \) and 7.
Figure 5 shows the thermomagnetic curves M(T) of the ribbon with x = 0 and x = 7 measured in low field of 20 Oe. We can see that when the temperature increases, the magnetization is abruptly reduced at Curie temperature T_C of amorphous phase. With further increasing temperature up to region of onset of crystallization, the \( \alpha \)-Fe(Si) crystallites start to be formed leading to the increase in magnetization. From M(T) curves, we define \( \Delta T = T_{onset} - T_C \) as the stabilizing temperature region of amorphous phase, in which no phase transition is detected (figure 5). T_C and \( \Delta T \) were determined for all samples and collected in table 2. Insert in figure 5 is the dependence of T_C and \( \Delta T \) of the samples versus Cr content substituted for Fe. The results show that T_C significantly decreased while \( \Delta T \) increased with increasing Cr content. It is clearly seen that we can control the working temperature of the ribbons by substitution effect and Cr plays the role of stabilizing amorphous structure.

The calculation of the magnetic entropy change, \( \Delta S_m \), associated with second-order phase transition was performed using the isothermal magnetization curves. Figure 6 shows the magnetization versus applied field up to 13.5 kOe at various temperatures of samples with x = 0 (figure 6a) and x = 7 (figure 6b). In our experiments, the changing rate of applied field is slow enough to get isothermal M-H curves.

In fact, \( \Delta S_m \) is often evaluated by some numerical approximation methods. One way of approximation is to directly use the measurements of the M(T) curve under different magnetic field. In the case of small discrete field intervals, \( \Delta S_m \) can be approximately determined from equation (1) as

\[
\Delta S_m = \sum \left[ \frac{\partial M}{\partial T} \right]_{H_i} \frac{1}{2} \Delta H_i
\]

where \( \frac{\partial M}{\partial T} \) is the experimental value obtained from M(T) curve in magnetic field H_i.

Another method is to use isothermal magnetization measurements. In the case of magnetization measurements at small discrete field and temperature interval, \( \Delta S_m \) can be approximately determined from equation (1) by

\[
\Delta S_m = \sum \frac{M_i - M_{i+1}}{T_{i+1} - T_i} \Delta H_i
\]

where M_i and M_{i+1} are the experimental values of the magnetization at T_i and T_{i+1}, respectively, under an applied magnetic field of H_i.
Figure 6. Magnetization as a function of applied field at different temperatures for the samples with x=0 (a) and x=7 (b).

Table 2. Curie temperature (T_C), stabilizing temperature region (ΔT) and the maximum value of magnetic entropy change (|ΔS_m|max) of the studied samples.

| Sample | x = 0 | x = 1 | x = 2 | x = 3 | x = 4 | x = 5 | x = 6 | x = 7 | x = 8 |
|--------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| T_C (K) | 450   | 425   | 400   | 375   | 355   | 330   | 310   | 300   | 280   |
| ΔT (K)  | 340   | 370   | 400   | 435   | 465   | 500   | 530   | 560   | 590   |
| |ΔH = 13.5 | 5.3   | 4.9   | 4.4   | 4.0   | 3.7   | 3.5   | 3.2   | 3.1   | 2.8   |
| ΔH = 10 | 4.9   | 4.6   | 4.2   | 3.8   | 3.4   | 3.2   | 2.6   | 2.5   | 2.1   |
| ΔH = 5  | 4.4   | 4.1   | 3.9   | 3.3   | 3.0   | 2.8   | 2.2   | 2.1   | 1.9   |

Figure 7. Magnetic entropy change of the studied samples with magnetic field variation of 13.5 kOe.

Figure 7 presents the temperature dependence of ΔS_m of the studied samples. It can be seen that the maximum value of |ΔS_m| occurs around T_C of amorphous phase and decreases with increasing Cr content. Namely, |ΔS_m| is of 5.3 J/kg.K and 2.8 J/kg.K measured in 13.5 kOe magnetic field variation for x = 0 and 8, respectively. ΔS_m has been also determined at lower field variation of 10 and 5 kOe and figure 8 shows the results for the ribbon with x = 7 as an example. It is interesting that the value of...
ΔSm|max reached the large value at the low field variation (see table 2). This can be only be explained in that our materials are ultrasmall magnetic materials. To our knowledge, these values of |ΔSm|max at magnetic field variation of 10kOe and 5kOe of the studied samples are the largest values that have not been reported so far. Especially, at magnetic field variation of 3 kOe, the value of |ΔSm|max of the samples is larger than 1 J/kg.K. Namely, |ΔSm|max is of 1.4 J/kg.K and 1.0 J/kg.K for x = 0 and 7, respectively. This has an important meaning for application that with the low magnetic field, the magnetic refrigerators only use a permanent magnet (AlNiCo, Nd_2Fe_14B) for a source of magnetic field.

From above mentioned results we could say that our studied materials have giant magnetocaloric effect working at a large temperature region (from under room temperature (280K) to high temperature (450K)) by moderate low magnetic field variation, thereby they are the best refrigeration materials at the present time.

The chemical anti-corrosion of Cr was also studied. The results show that the mass of the samples without Cr or with less Cr content (x = 0÷2), strongly decreases with time when they are soaked in the solution of diluted brine (concentration c = 5‰), while the mass of the samples with higher Cr content is almost constant. The results are shown in figure 9. This can be only explained due to the anti-corrosion ability of Cr. So, the sample containing Cr can work in the breaking environments (seawater, acid, alkali...).

4. Conclusions
Magnetic ribbons of composition Fe_{78-x}Cr_xSi_4Nb_5B_{12}Ag_4 are prepared by rapid quenching technology with amorphous structure. Cr substitution makes increasing crystallization temperature of α-Fe(Si) phase and crystallization activation energy, shifting the Curie temperature of amorphous phase to room temperature region as well as stabilizing amorphous structure of samples. The large magnetocaloric effect (GMCE) has been established in all studied samples at low field variation. This has an important meaning for application with the low magnetic field, for example when the magnetic refrigerators only use a permanent magnet (AlNiCo, Nd_2Fe_14B) for a source of magnetic field. It is convinced that the studied samples have combined a number of advantages of magnetocaloric materials. Therefore they are the best materials working for active magnetic refrigeration at large temperature range from room to high temperature region. After appropriate annealing, materials become nanocomposites with ultrasoft magnetic properties. The existence of Cr increases the chemical anti-corrosion ability of the samples and these samples can be used in the breaking environments (seawater, acid, alkali...).

References
[1] Warburg E 1981 *Ann. Phys.* 13 141
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