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Magnetocaloric effect in amorphous and partially crystallized Fe_{40}Ni_{38}Mo_{4}B_{18} alloys

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A study of magnetocaloric effect in amorphous and partially crystallized Fe_{40}Ni_{38}Mo_{4}B_{18} alloys is reported. Amorphous Fe_{40}Ni_{38}Mo_{4}B_{18}, near its magnetic ordering temperature (600K) showed a magnetic entropy change $\Delta S_M$ of 1.1 J/KgK and a relative cooling power of 36J/Kg in a field change of 10 kOe. Amorphous samples were partially crystallized by annealing at 700 K at different time intervals. Partially crystallized samples showed two distinct magnetic ordering temperature, one corresponding to the precipitated FeNi nanocrystals and the other one corresponding to the boron rich amorphous matrix. Magnetic ordering temperature of the residual amorphous matrix got shifted to the lower temperatures on increasing the annealing duration. Partially crystallised samples showed a magnetic entropy change of about 0.27J/kgK near the magnetic ordering temperature of the amorphous matrix (540K) in a field change of 10 kOe. The decrease in $\Delta S_M$ on partial crystallisation is attributed to the biphasic magnetic nature of the sample. © 2016 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).

I. INTRODUCTION

The quest for new materials that would help us improve our life quality has always been an active area of research. In this time of environmental challenges it is necessary that we should adhere to technologies that will not harm nature. The idea of magnetocaloric effect (MCE) stems from this notion and there had been tremendous research on this direction that yielded many promising magnetocaloric materials (MCM). The temperature change associated with a material which undergoes an adiabatic change in magnetic field is known as MCE and materials exhibiting this property are called magnetocaloric materials. Using MCE, if we could achieve reasonable temperature change near room temperature this would enable to materialise a magnetic refrigerant which is energy efficient as well as environmental friendly. This makes the search for novel MCM an intense topic of research. Important parameters characterising a MCM are magnetic entropy change ($\Delta S_M$) and relative cooling power (RCP). Despite having largest $\Delta S_M$, Gd based compounds are not favoured by researchers since they are expensive and scarce. Moreover MCM with first order phase transition (FOPT) (Gd_{5}Si_{1.7}Ge_{2.3}, MnFeP_{0.45}As_{0.55} etc.) shows hysteresis losses (both magnetic and thermal) which will limit the performance of a refrigerator employing this material. The commercial application of MCMs requires tunable Curie temperature $T_C$, reasonable MCE and good RCP. In this context amorphous alloys could be useful MCMs as they offer affordable material and fabrication costs, reasonable MCE, low hysteresis loss, high electrical resistivity and tunable $T_C$. 

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The soft magnetic alloys are good candidates for MCE based cooling applications as they have large enough magnetisation and are relatively free of hysteresis. Besides there are many reasons people opt for amorphous magnetic materials in their search for better MCM. They show broad $\Delta S_M$ peak around $T_C$, which is a second order phase transition. Alloying provides an easy way of tuning $T_C$. They have good mechanical properties and high corrosion resistance and also produce large RCP. Recent studies on rare-earth free nanoparticles for magnetocaloric applications have shown that it is tangible to achieve near room temperature magnetic transitions by suitable combination of materials as well as the accompanied RCP of these systems are found to be greater than the benchmark material Gd.

Fe$_{40}$Ni$_{38}$Mo$_4$B$_{18}$ alloys (commercially named as METGLAS 2826MB) are well known for their sensor and soft magnetic applications owing to their very soft magnetic properties and amorphous structure. There has been very little discussion of the MCE behaviour of FeNiMoB amorphous alloys. FeZrBCu, FeBCrGd, FeCoCrZrB alloys have been studied to understand how mechanical alloying affects MCE behaviour of the system. Certain approaches exist to study the effect of annealing temperature on the magnetocaloric properties of the amorphous ribbons. In this paper it will be shown that the partial crystallisation plays a vital role in determining the $\Delta S_M$ and RCP values of the amorphous alloy with composition Fe$_{40}$Ni$_{38}$Mo$_4$B$_{18}$. The present investigation revealed that FeNiMoB alloy possess entropy change comparable with its counterparts. It even transcends alloys containing rare earth elements as well as several other Fe based amorphous alloys.

II. EXPERIMENTAL

Commercially available amorphous alloy of nominal composition Fe$_{40}$Ni$_{38}$Mo$_4$B$_{18}$ was annealed at 700 K for different duration 15 min, and 45 min in high vacuum conditions ($<10^{-4}$ torr) offered by a physical property measurement system (Dynacool, Oven option). Different time intervals were chosen for annealing so that a control over microstructure was possible. Annealing temperature was chosen from the differential scanning calorimetry (DSC) studies depicted in Fig. 1. The temperature for primary crystallisation was obtained from this data and the onset of crystallization was around 675K. For annealing experiments, the heating and cooling rate was fixed to 20K/min. The X-ray diffraction pattern of the samples were collected using PANalytical X’Pert Pro diffractometer operated at 40 kV and 30 mA (Cu-K$\alpha$ radiation). The diffraction measurements were performed in the 2$\theta$ range 10$^\circ$–90$^\circ$. Magnetic properties were measured using VSM option of the Physical Property Measurement System (Quantum Design, Dynacool). Magnetisation as a function of field was recorded in fields upto 10 kOe at 1 K interval in the critical region ($\sim T_C$ ± 12 K) and

![FIG. 1. DSC result of melt spun Fe$_{40}$Ni$_{38}$Mo$_4$B$_{18}$.](image-url)
at 5K intervals outside the critical region. Before proceeding to M-H measurements, the sample was cycled in the temperature range 300-625 K until no shift in $T_C$ was observed. This procedure ensured that the structural relaxation do not affect the magnetization data. Moment as a function of temperature was measured in a small but constant applied field of 50 Oe. $T_C$ was determined from the $\frac{dM}{dT}$ vs. T curve and for amorphous Fe$_{40}$Ni$_{38}$Mo$_4$B$_{18}$ it was found to be $\sim$600K.

III. RESULTS AND DISCUSSIONS

A. Structure

The XRD patterns of as prepared and samples annealed at 700 K for different time intervals are presented in figure 2. Samples are christened as t0 (unannealed), t15 (annealed for 15 min), and t45 (annealed for 45 min). XRD of as prepared sample shows a broad peak located at $\sim$44$^\circ$, indicating short range atomic correlations in this alloy. On annealing, the peak centred at $\sim$44$^\circ$ gets narrower indicating that the amorphous phase is gradually transforming to a nanocrystalline phase. Our previous studies have shown that amorphous Fe$_{40}$Ni$_{38}$Mo$_4$B$_{18}$ alloy partially crystallises upon annealing.$^{23-25}$ In that study the variation of crystal number density with heat treatment time at different heat treatment temperatures was presented. It was revealed that the crystal number density increased with an initial increase in heat treatment time and reached a steady state value after prolonged annealing time. This steady state value of volume fraction increases with increasing heat treatment temperature. Similarly, average crystallite size also increased initially with an increase in heat treatment time and reached a constant value after 4 h of annealing.$^{24}$ It was also concluded that the product of primary and secondary crystallization for this alloy are Fe–Ni solid solution and (FeNiMo)$_{23}$B$_6$ respectively.$^{23}$ The annealing temperature of 700K in the present case is well below the secondary crystallisation temperature of this alloy. On annealing amorphous FeNiMoB alloy at a temperature close to its primary crystallisation temperature, partial crystallisation will be initiated. In this case, nanoscale fcc Fe-Ni crystals will be formed in an amorphous matrix by a homogeneous and transient nucleation. The microstructure of the partially crystallised FeNiMoB alloy therefore resembles that of nanocrystalline fcc-Fe-Ni grains embedded in a boron rich amorphous matrix. On increasing the annealing time, crystal volume fraction as well as size increases which results in a narrowing of diffraction peak at around 44$^\circ$. The crystallization of alloy is dictated by the metalloid present in it. Earlier studies have concluded that the elements like Mo and B are rejected by the primary phase fcc Fe-Ni causing a concentration gradient at the crystal-matrix interface. The rejected Mo and B atoms will diffuse into the remaining amorphous phase. It is expected that B diffuses much faster than Mo into the amorphous matrix. The concentration gradient of B and Mo atoms will result in Mo piling up at the crystal-matrix interface. Mo at the crystallite boundary to

![FIG. 2. XRD of amorphous ribbon (t0) as well as those annealed at different time intervals (t15, t45).](image-url)
some extent inhibits the crystal growth. On the other hand the B content of the amorphous matrix keep on increasing with increasing annealing time/crystallite volume fraction.24

B. Magnetic properties of amorphous FeNiMoB

Figure 3(a) shows the temperature dependence of magnetization (M-T) of FeNiMoB amorphous alloy measured in an applied magnetic field of 50 Oe. The curve shows a sharp transition from a ferromagnetic to a paramagnetic state at around the ordering temperature $T_C = 600K$.

The isothermal magnetization curves for amorphous sample taken at temperature interval $\Delta T = 5$ K is depicted in figure 3(b). The M-H results has been used to calculate the entropy change associated with the amorphous alloy. The entropy change $\Delta S_M$ associated with an adiabatic magnetic change is given by Maxwell relation

$$\Delta S_M = \int_0^{H_1} \left( \frac{\partial M}{\partial T} \right) dH$$

where the partial derivative is replaced by finite differences and numerical integration is performed. The magnetic entropy change, determined from the isothermal magnetization data, is shown as a function of temperature in figure 4. The peak entropy change is observed around $T_C$ and the value obtained is 1.13 J/kgK. Further, RCP is also determined for the amorphous sample using the relation

$$RCP = \left| \Delta S_M^{max} \right| \frac{\delta T_{FWHM}}{26}$$

FIG. 4. $\Delta S_M$ vs $T$, solid line is a guide to eye.
Here $\delta T_{FWHM}$ is the full width at half maximum of the $\Delta S_M$ vs $T$ curve. RCP is the measure of the amount of heat that can be transferred between the cold and hot reservoirs in an ideal refrigeration cycle and the value is found to be 36 J/kg.

In order to understand MCE in this amorphous alloy, the nature of the magnetic phase transition responsible for the MCE needs to be determined. According to Banerjee criteria,\textsuperscript{27} the order of the magnetic phase transition can be determined from the slope of the Arrot plot. Figure 5(a) is an Arrott plot ($M^2$ vs $H/M$) constructed by assuming critical exponents, $\beta=0.5$ and $\gamma=1$. A positive slope in this figure gives testimony to the fact that the phase transition in this amorphous alloy is a second order PM-FM phase transition. According to mean field theory, the $M^2$ vs $H/M$ plots around $T_C$ should be a series of parallel straight lines and at $T_C$, the straight line should pass through the origin. However, the assumption of $\beta=0.5$ and $\gamma=1$, resulted in a non linearity in $M^2$ vs $H/M$ at $T\sim T_C$, showing that the mean field model is not valid in the present case. Based on scaling hypothesis, a second order magnetic phase transition near Curie temperature is characterised by a set of critical exponents $\beta$, $\gamma$, and $\delta$. To determine the critical exponents and $T_C$ of our samples, we analyzed the M(H) data according to the modified Arrott plot (MAP) method based on the Arrott-Noakes equation of state.\textsuperscript{28} The critical exponents $\beta$, $\gamma$, and $\delta$ obey the following relations\textsuperscript{29}

$$M_S(T) = M_0(-\epsilon)^{\beta}, \quad \epsilon < 0$$

$$\chi_0^{-1}(T) = \frac{h_0}{M_0(\epsilon)^{\gamma}}, \quad \epsilon > 0$$

$$M = DH^{1/3}, \quad \epsilon = 0$$

where $\epsilon$ is the reduced temperature $(T - T_C)/T_C$ and $M_0$, $h_0$ and $D$ are the critical amplitudes. In this method isothermal magnetization data taken at different temperatures are used to construct
$M^{1/β}(H/M)^{1/γ}$ plot and the values of $β$, and $γ$, are varied so as to make these isotherms linear over a wide range of $H/M$ values as possible and parallel to each other in a narrow temperature region around $T_C$.\cite{30,31} The values of critical exponents are calculated using modified Arrott plot (MAP) method. The temperature range over which critical exponents determined is so chosen that it falls well within the asymptotic critical region (ACR). During the course of critical exponent analysis the temperature range around $T_C$ is so narrowed down to the extent that $|ε|-10^{-2}$. In this respect, although the critical exponents determined are still effective exponents, their values are very close to the asymptotic ones. The values of $β$, $γ$ and $δ$, are calculated to be 0.338(18), 1.346(79) and 4.86(42) respectively for $T = 599±1$K. Figure 5(b) shows the modified Arrott plot that has been drawn using newly found critical exponents. With the $β$ and $γ$ values thus obtained, $M^{1/β}$ versus $(H/M)^{1/γ}$ curves at high fields around $T_C$ are parallel straight lines.

Validation of thus obtained critical exponents is necessary. According to scaling theory,\cite{32} the critical behaviour of the system can be written as

$$M(H, ε) e^{-β} = f_+(H/ε^{β+γ})$$

(6)

where $ε$ is the reduced temperature $(T-T_C)/T_C$ and $f_+$ for $T>T_C$ and $f_-$ for $T<T_C$ are regular functions.\cite{32} This equation implies that the performance of the $M e^{-β}$ versus $H/ε^{β+γ}$ makes all M(H) data points falling into two universal branches characteristic of $f_+$ for $T>T_C$ and $f_-$ for $T<T_C$. For our case, by plotting the $M e^{-β}$ versus $H/ε^{β+γ}$, using the critical exponents and $T_C$ obtained from the modified Arrott plots method, one can see that all the data points fits into two universal branches with $T>T_C$ and $T<T_C$ (fig 5(c) and 5(d)). Please note that the same quality of data collapse onto two universal curves can be achieved for a wide range of parameter values (typically ±2% for $T_C$ and 10% for $β$ and $γ$) particularly when the data outside the ACR are also included in the analysis.\cite{33} A possible way to tackle this problem is to exclude data taken at temperatures away from $T_C$, so that the exponents $β$ and $γ$ become increasingly sensitive to the choice of $T_C$.\cite{31}

In the present study we have taken care to do scaling equation of state analysis in the asymptotic critical region of the amorphous alloy. In this regard, the ferromagnetic behaviour around the Curie temperature was properly renormalized following the scaling equation of state, indicating that the present exponents are reasonably accurate. The values of critical exponents’ $β$, $γ$, and $δ$ determined as described above take us to conclude that the amorphous system agrees upon 3D Heisenberg model in which nearest neighbour interaction is taken into account.

Around $T_C$ the peak entropy change is observed and the value obtained is 1.13J/kgK. This value is comparable with other amorphous alloy Fe-Co-Cr-Zr-B.\cite{19} Although the peak value of $ΔS_M$ is good it has a low RC$_{FWHM} (36J/kg)$. It is important to note that for magnetic refrigeration application, the relative cooling power computed from the adiabatic temperature change is essential. For this, specific heat data at different temperatures and magnetic fields are needed.\cite{35} Such a measurement was not possible in the present study due to the experimental limitations imposed by higher ordering temperatures (greater than 400K). Table 1 gives a comparison of MCE properties of Fe-Ni-Mo-B alloy with other Fe-B based amorphous alloys.

### C. Magnetic properties of nanocrystalline FeNiMoB

Fig 6(a) shows magnetisation as a function of temperature measured in a field of 50 Oe, for samples annealed at 15 and 45 minutes. It is clear that the M-T curve for the nanocrystalline sample shows behaviour typical for a material containing two ferromagnetic phases. Unlike amorphous ribbon, each of the annealed samples has two different transitions corresponding to $T_C$ of amorphous phase ($T_{C}^{am}$) and $T_C$ of crystalline phase ($T_{C}^{cr}$) respectively (see fig 6(b)). As discussed earlier, the crystalline phase is fcc-FeNi and amorphous phase is rich in boron. Generally, regarding the case of Fe based amorphous alloys one would expect an increase in $T_{C}^{am}$ while moving from amorphous to partially crystalline alloys.\cite{2} We could ascribe this to two factors 1) the effect of crystallite and 2) inhomogeneous spatial distribution of metalloid atoms at the amorphous interphase.\cite{34} In the former case, it was suggested that the exchange coupling between the ferromagnetically ordered
TABLE I. MCE properties of some Fe-B based amorphous alloys.

| Alloy                  | $\Delta S_m$ (J/kgK) | $R_{FWHM}$ (J/kg) | Field change (T) | Reference |
|------------------------|-----------------------|--------------------|------------------|-----------|
| Fe$_{88}$Zr$_7$B$_4$Cu$_1$ | 1.3                   | 165                | 1.5              | 4         |
| Fe$_{82}$Co$_{2.75}$Ni$_{1.75}$Zr$_7$B$_4$Cu$_1$ | 1.4                   | 164                | 1.5              | 4         |
| Fe$_{77}$Co$_{5.5}$Ni$_{5.5}$Zr$_7$B$_4$Cu$_1$ | 1.8                   | 128                | 1.5              | 4         |
| Fe$_{71}$Co$_{8.75}$Ni$_{8.75}$Zr$_7$B$_4$Cu$_1$ | 2                     | 130                | 1.5              | 4         |
| Fe$_{68}$Co$_{15}$Cr$_{10}$Zr$_7$B$_4$Cu$_1$ | 0.95                  | 102                | 1.1              | 2         |
| Fe$_{68}$Zr$_{12}$B$_{12}$ | 0.92                  | 70                 | 1.1              | 2         |
| Fe$_{81.6}$Mo$_{0.75}$Zr$_{1.3}$Nb$_{0.75}$B$_{6.8}$Cu$_{1}$ | 0.75                  | -                  | 1               | 3         |
| Fe$_{9}$Zr$_{12}$B$_{12}$ | 0.75                  | 54                 | 1                | 22        |
| (Fe$_{90}$Co$_{5}$Cr$_{5}$)$_{1}$Zr$_{12}$B$_{12}$ | 1.3                   | 53                 | 1                | 22        |
| (Fe$_{65}$Co$_{10}$Cr$_{5}$)$_{1}$Zr$_{12}$B$_{12}$ | 1.4                   | 32                 | 1                | 22        |
| (Fe$_{65}$Co$_{10}$)$_{1}$Zr$_{12}$B$_{12}$ | 1.1                   | 38                 | 1                | 22        |
| (Fe$_{75}$Co$_{15}$Cr$_{5}$)$_{1}$Zr$_{12}$B$_{12}$ | 1                     | 43                 | 1                | 22        |
| Fe$_{81}$Nb$_{12}$ | 0.75                  | -                  | 0.7              | 14        |
| Fe$_{77.5}$Cr$_{3.5}$Nb$_{3}$B$_{12}$ | 0.73                  | -                  | 0.7              | 14        |
| Fe$_{66.5}$Mo$_{0.75}$Si$_{13.5}$B$_{6.8}$Cu$_{1}$ | 1.1                   | 110                | 1.5              | 15        |
| Fe$_{71.5}$Cr$_{3.5}$Nb$_{3}$B$_{6.8}$Cu$_{1}$ | 0.45                  | -                  | 0.6              | 16        |
| Fe$_{2}$Cr$_{3}$Nb$_{3}$B$_{6.8}$Cu$_{1}$ | 0.55                  | -                  | 0.6              | 16        |
| Fe$_{4}$Ni$_{2}$Mo$_{0.75}$B$_{11}$ | 1.1                   | 36                 | 1                | This work |

atoms of the crystallites and the atoms of the matrix induces ferromagnetism on the layers of the matrix adjacent to the interface, and through the exchange coupling, the magnetic order propagates inwards toward the matrix, giving rise to a spontaneous magnetization above its Curie temperature. However, in the present study we have seen that as a consequence of crystallization, $T_{C}^{am}$

FIG. 6. a) Temperature dependence of magnetization for sample t15 and t45 measured in a field of 50 Oe b) $dM/dT$ as a function of temperature c) M-H isotherms measured at different temperatures for sample t15 and d) sample t45.
is shifted to low temperature region. This is explained by considering the following points 1) the crystallite volume fraction may be too low that there is sufficient amount of amorphous phase which is exchange decoupled with the precipitated crystallites 2) inter-atomic distance dependency of the exchange integral $J(\tilde{r}_1)$ and the ordering temperature $T_C$. Here $\tilde{r}_1$ is the mean metal-metal inter-atomic distance. In amorphous phase, structural fluctuations give rise to fluctuations in the exchange interactions. Considering the fact that $J(\tilde{r}_1)$ in nickel based alloys lies in the right side of the peak of the Bethe–Slater curve, a slight increase in the metal-metal inter-atomic distance by the addition of metalloid will reduce $J(\tilde{r}_1)$ and therefore $T_C$. It is also to be noted that the as prepared amorphous ribbon showed a sharp change in magnetisation near $T_C\sim 600K$. This is because of the uniformity in exchange coupling constant between transition metal atoms. Once nanocrystallisation occurs, the residual amorphous matrix becomes depleted of Fe and Ni and rich in B. This creates a distribution of $J(\tilde{r}_1)$ in the residual amorphous matrix because of the dilution of Fe and Ni. Therefore, the change in M near $T_C^{am}$ in nanocrystalline sample becomes gradual. As more Fe-Ni crystals are precipitated as expected in the case of t45, $T_C^{am}$ gets shifted to low temperature as well as the transition gets broadened.

Figure 6(c) and 6(d) shows the magnetic isotherms recorded for sample t15 and t45 at different temperatures below and above the respective $T_C^{am}$.

The magnetic entropy change associated with these nanocrystalline alloys is calculated using eqn (1). Figure 7 portraits variation of entropy with temperature for sample t15 and t45. MCE of the system is found to be decreasing with crystallization. It is found that both, peak $\Delta S_M$ and RCP, decreased when the system undergoes partial crystallization. The figures characterising MCE of amorphous and partially crystallized alloys are presented in table II.

As evidenced from figure 4 the high value of $\Delta S_M$ in amorphous sample near $T_C^{am}$ compared to nanocrystallized samples can be correlated to sharp change of magnetization with respect to temperature. Despite having a low value for RCP, the merit of FeNiMoB alloy lies in the fact that it has a very good value of entropy change compared to other alloys of its kind (see table I). It is noteworthy that the entropy change associated with FeNiMoB amorphous ribbon is comparable with other alloys containing rare-earth elements such as FeBCrGd. Moreover the value of $\Delta S_M$ is promising as it is obtained for a field change of 10 kOe.

**TABLE II.** Properties characterising MCE of FeNiMoB.

| Sample   | $T_C$ (K) | Entropy change (J/kgK) | RCP (J/kg) |
|----------|-----------|------------------------|------------|
| Amorphous| 600       | 1.13                   | 36         |
| t15      | 575       | 0.36                   | 20         |
| t45      | 540       | 0.27                   | 25         |
IV. CONCLUSIONS

Magnetocaloric effect of Fe$_{40}$Ni$_{38}$Mo$_0$B$_{18}$ amorphous alloy and its dependence on partial crystallisation is studied. Fe$_{40}$Ni$_{38}$Mo$_0$B$_{18}$ amorphous alloy showed a magnetic entropy change of 1.1 J/KgK and a relative cooling power of 36J/Kg in a field change of 10 kOe at 600K. The entropy change $\Delta S_M$ associated with FeNiMoB alloy decreased with crystallization since the Fe, Ni content in the residual amorphous phase was decreased. RCP of the system was also reduced after annealing due to sluggish paramagnetic to ferromagnetic transition which is caused by the concentration fluctuations in the residual amorphous phase. Critical exponents determined show that the amorphous alloy belongs to the 3D Heisenberg class. Fe$_{40}$Ni$_{38}$Mo$_0$B$_{18}$ alloy can be considered as a material for high temperature magnetic refrigeration applications such as localised cooling at high temperatures like in aircraft and other military systems, where access to conventional cooling systems or cold heat sinks is not available.

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