The influence of Dy additions on the magnetocaloric effect in $Gd_{0.97}V_{0.03}$ alloys

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ABSTRACT

The influence of Dy on the magnetocaloric effect in $Gd_{0.97-x}Dy_xV_{0.03}$ (x=0.1, 0.2, 0.3) alloys has been studied. These alloys were prepared by arc melting on a water-cooled copper hearth under an argon atmosphere. The magnetization behavior has been analyzed by X-ray diffraction and a vibrating sample magnetometer. Results indicate that the Curie points of $Gd_{0.97-x}Dy_xV_{0.03}$ alloys decrease linearly with increasing content of Dy. The values of maximum magnetic entropy change (ΔS_M) and relative cooling power (RCP) for $x=0\sim0.2$ is larger than that of Gd alone over a wider temperature range. The $Gd_{0.97-x}Dy_xV_{0.03}$ alloys have promising potential as working substance candidates for magnetic refrigeration due to their tunable Curie temperature and the favorable properties of the magnetocaloric effect.

1. Introduction

Recently, magnetic refrigeration is becoming increasingly attractive due to its high efficiency, energy saving and environmental concerns, compared with the conventional vapor-cycle refrigeration [1,2]. Considerable research and development efforts have been employed to produce magnetic refrigerating materials for use in the near room temperature region. Magnetic refrigeration is based on the magnetocaloric effect (MCE), which describes the adiabatic temperature change of materials produced by the magnetic entropy change upon the application and removal of a magnetic field [3]. Isothermal magnetic entropy change ΔS and adiabatic temperature change ΔT_{ad} are two basic factors which are used as figures of merit of the MCE of magnetic refrigerating materials. Gadolinium is considered historically to be the optimal working substance as a room temperature magnetic refrigerant, because its magnetic entropy change ΔS is near room temperature(maximum magnetic entropy change ΔS_M=5.0 J/kg K) under a magnetic field change of 0∼2 T at the Curie temperature (T_c=293 K). However, the large entropy of Gadolinium exists only in a very narrow temperature range [4], which means that a refrigeration cycle is achieved only within this narrow temperature range. Accordingly, it is difficult for such a material to deliver stable operation over a large refrigeration temperature difference [5].

The magnetic, electrical and thermal properties of several binary $Gd_{1-x}R_x$ compounds (R=Tb, Cu, Cr, B, C, In and Co) were studied in Refs [6–11]. Zhang et al. found that adding either Tb and Nd can lower the Curie temperature of $Gd_{1-x}R_x$ and that small additions of Nd (∼5%) have only a slight influence on the MCE of the $Gd_{1-x}Tb_x$ alloy. Wang et al. reported that additions of B to Gd (2, 5 and 7 at.%) expanded the unit cell volume, raised T_C by 4 K to 298 K, increased the refrigeration capacity, q, by 12% and had no effect on ΔS_M. But these binary $Gd_{1-x}R_x$ alloys remain limited because they have no large entropy change over a wider working temperature.

We have previously studied the magnetic properties and magnetic entropy changes of $Gd_{1-x}V_x$($x=0\sim0.1$) alloys. It is noted that $Gd_{99.7}V_{0.03}$ alloys have large values of ΔS_M and broader peaks in the ΔS_{M-T} plot in low magnetic fields, and its refrigerant capacity is better than that of Gd. To explore these

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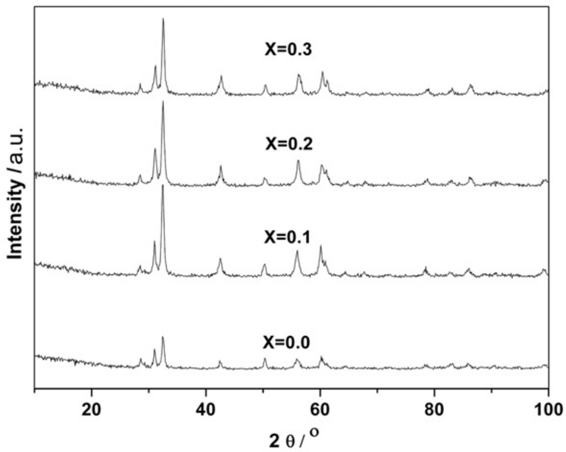

Fig. 1 – X-ray diffraction patterns for $Gd_{0.97-x}Dy_xV_{0.03}$ alloys with $x=0$, 0.1, 0.2 and 0.3.

effects further, we report the effect of substitution of Dy for Gd on the MCE in $Gd_{99.7}V_{0.03}$ alloys. We anticipated that the addition of a small amount of Dy atoms would lead to a decrease of the Curie temperature, without losing the large MCE.

2. Experiments

The $Gd_{0.97-x}Dy_xV_{0.03}$ ($x=0.1$, 0.2, 0.3) samples were prepared by arc melting on a water-cooled copper hearth under an argon atmosphere. Each sample was arc melted six times with the button turned over each time to ensure homogeneity. The melted buttons were wrapped in Ta foil, sealed under argon in quartz tubes, annealed at 1100 °C for 48 h, followed by a quench to room temperature. Structural analysis was made by X-ray diffraction using Cu–Kα radiation. Magnetic measurements were performed with a vibrating sample magnetometer (VSM) in fields up to 2.0 T. The magnetic entropy change is calculated from isothermal magnetization measurements, and the adiabatic temperature change is measured in an instrument which is installed in a 1.4 T field built by Xihua University (Chengdu, China).

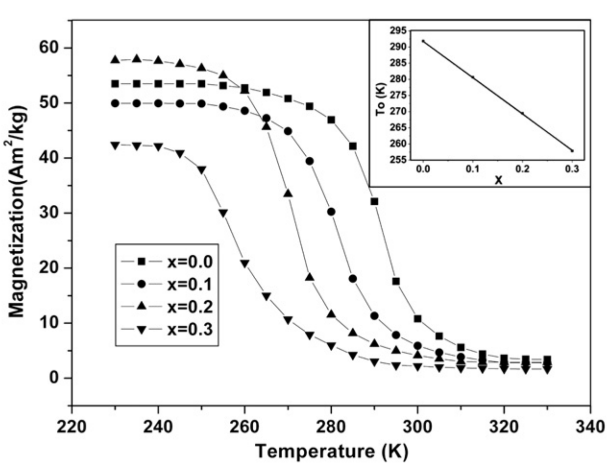

Fig. 2 – Temperature dependence of the magnetization (M–T) curves for $Gd_{0.97-x}Dy_xV_{0.03}$ alloys with $x=0$, 0.1, 0.2 and 0.3 measured in an applied field of 100 Oe.

Table 1 – Curie temperature (T_C), magnetic entropy change (ΔS_M), half maximum of the entropy change peak (δT_H) and refrigerant capacity (RCP) of $Gd_{0.97-x}Dy_xV_{0.03}$ alloys

Sample	T_C/K	ΔS_M/J kg^{-1}K^{-1}	δT_H/K	RCP/J kg^{-1}
Gd	293.00	5.00	38.6	193.00
$Gd_{0.97}V_{0.03}$	291.84	5.19	44.8	232.51
$Gd_{0.87}Dy_{0.1}V_{0.03}$	280.66	4.96	40.4	200.38
$Gd_{0.77}Dy_{0.2}V_{0.03}$	269.48	5.33	35.4	188.68
$Gd_{0.67}Dy_{0.3}V_{0.03}$	257.84	4.15	35.4	146.91

3. Results and Discussion

Fig. 1 shows the X-ray diffraction patterns for the $Gd_{0.97-x}Dy_xV_{0.03}$ alloys with $x=0$, 0, 0.1, 0.2 and 0.3. According to Fig. 1, it was difficult to discern phases other than the hexagonal structure of Gd. The Gd-rich side of the Gd-V system had been studied by Baenziger et al. [12], who reported that no intermediate phases were found in this system. This suggested that the V atoms were dissolved in Gd metal, and the patterns for these alloys were coincident with those of the solid solution.

The temperature dependence of the magnetization (M–T curves) for $Gd_{0.97-x}Dy_xV_{0.03}$ alloys with $x=0$, 0.1, 0.2 and 0.3 was measured in an applied field of 100 Oe over the temperature range from 230 K to 330 K; results are shown in Fig. 2. The values of T_c determined from the M–T curves are listed in Table 1. From the plot (Fig. 2, inset), we knew that the values of T_c decreased linearly with increasing Dy content, which implied that the Curie points were tunable by changing x in the $Gd_{0.97-x}Dy_xV_{0.03}$ alloys. This property is very important because it ensures these alloys will perform over the different temperature regions in a magnetic refrigerator.

Isothermal M–H curves of $Gd_{0.97-x}Dy_xV_{0.03}$ alloys were measured in the magnetic field range of 0 ~ 2.0 T at different temperatures in the vicinity of the Curie temperature with 5 K increments. To determine the type of the phase transition for these alloys, the measured data for the M–H isotherms were

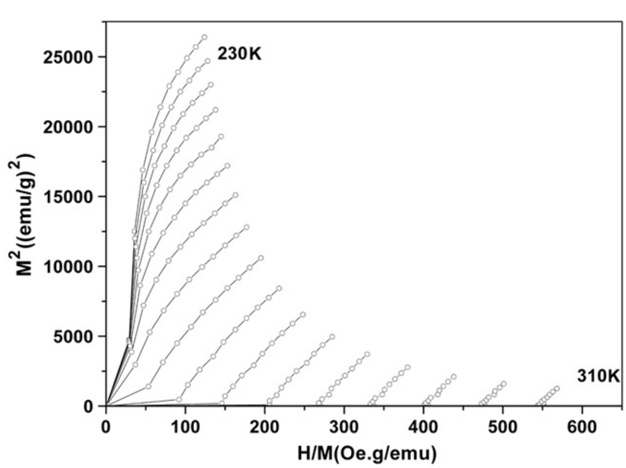

Fig. 3 – The H/M vs. M^2 plots for the isotherms of $Gd_{0.77}Dy_{0.2}V_{0.03}$.