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Magnetocaloric response of amorphous and nanocrystalline Cr-containing Vitroperm-type alloys

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ABSTRACT

The broad compositional range in which transition metal (TM) based amorphous alloys can be obtained, yields an easily tunable magnetocaloric effect (MCE) in a wide temperature range. In some TM-based alloys, anomalous behaviors are reported, as a non-monotonous trend with magnetic moment (e.g. FeZrB alloys). Moreover, in certain Cr-containing Vitroperm alloys anomalously high values of the magnetic entropy change were published. In this work, a systematic study on MCE response of Cr-containing amorphous alloys of composition $Fe_{74-x}Cr_xCu_1Nb_3Si_{15.5}B_{6.5}$ (with x=2, 8, 10, 12, 13, 14 and 20) has been performed in a broad Curie temperature range from 100 K to 550 K. Curie temperature and magnetic entropy change peak of the amorphous alloys decrease with the increase of Cr content at rates of −25.6 K/at% Cr and −54 mJ kg^{-1} K^{-1}/at% Cr, respectively, following a linear trend with the magnetic moment in both cases. The presence of nanocrystalline phases has been considered as a possible cause in order to explain the anomalies. The samples were nanocrystallized in different stages, however, the magnetocaloric response decreases as crystallization progresses due to the large separation of the Curie temperatures of the two phases.

1. Introduction

Magnetic refrigeration is called to be an energetic efficient green alternative to the usual refrigeration systems based on the compression-expansion of gasses. Magnetic refrigeration is based on the magnetocaloric effect (MCE), defined as the temperature change under a magnetic field variation in an adiabatic process (ΔT_{ad}) or as the magnetic entropy change in an isothermal process due to a magnetic field variation (ΔS_M) [1]. From Maxwell relations ΔS_M can be expressed as:

$$\Delta S_M = \mu_0 \int_0^H (\partial M/\partial T)_H \mathrm{d}H$$

where M, T, H and μ_0 are the magnetization, temperature, magnetic field and magnetic permeability of vacuum, respectively. From that, it is deduced that the MCE is maximum around a phase transition which implies magnetization changes, either with first (FOPT) or second order (SOPT) character. FOPT materials show high magnetocaloric peaks but in a narrow temperature range. Moreover, they normally present associated hysteresis phenomena. On the other hand, SOPT materials show smaller magnetocaloric peaks but in a wider temperature range than FOPT materials and without associated hysteresis. In this sense, transition metal (TM) based amorphous alloys have been widely studied since they were proposed as low cost candidates for magnetocaloric applications due to the easily tuned Curie temperature (T_C), negligible magnetic hysteresis, high electrical resistivity (decreasing eddy current losses) and excellent mechanical properties [2–5]. In addition to this potential for applications, they constitute model systems in which detailed studies of the different magnitudes affecting magnetocaloric response could be analyzed, like scaling of the properties [6], influence of demagnetizing field [7] or interphase interactions [8], etc.

The MCE response of Cr-containing amorphous alloys has been reported with extremely high values [9]. However, these values are not in agreement with other data found in the literature [10–12]. These anomalies could be due to a non-monotonous behavior of the magnetic moment with the addition of different elements in the amorphous matrix (as it has been found for FeZrB alloys [13]) or to a composite character of the system [14]. In this work, a

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systematic study on the MCE response of a Cr-containing amorphous alloy series has been performed. This series extends in a very broad Curie temperature range, from ~100 K to 550 K. The possible causes of the described anomalies are explored.

2. Experimental

Ribbon samples of composition $Fe_{74-x}Cr_xCu_1Nb_3Si_{15.5}B_{6.5}$ (with x=2, 8, 10, 12, 13, 14 and 20) were produced by melt spinning. Throughout the paper, samples are referenced by its Cr content. Microstructural characterization of the samples was done by X-ray diffraction (XRD) experiments with Cu Kα radiation in a Bruker D8I diffractometer. The study of the thermal stability and the heat treatments of the samples was performed by differential scanning calorimetry (DSC) in a Perkin–Elmer DSC7 under Ar flow. Magnetic measurements were performed in a Lakeshore 7407 vibrating sample magnetometer (VSM) equipped with a cryostat down to 77.7 K or an oven up to 1300 K. Samples with ~25 μm of thickness were cut as discs of 3 mm diameter to minimize the effect of the demagnetizing factor and sample positioning. The mass of the samples was measured in a Mettler Toledo XP26 scale with an accuracy of 1 μg. Magnetocaloric analysis has been performed using the software Magnetocaloric Effect Analysis Program [15], available from LakeShore Cryotronics Inc.

3. Results

Fig. 1 shows the XRD patterns of the as-quenched Cr-containing Vitroperm ribbons in which it can be observed that samples are fully amorphous, independently of the Cr content. Concerning the

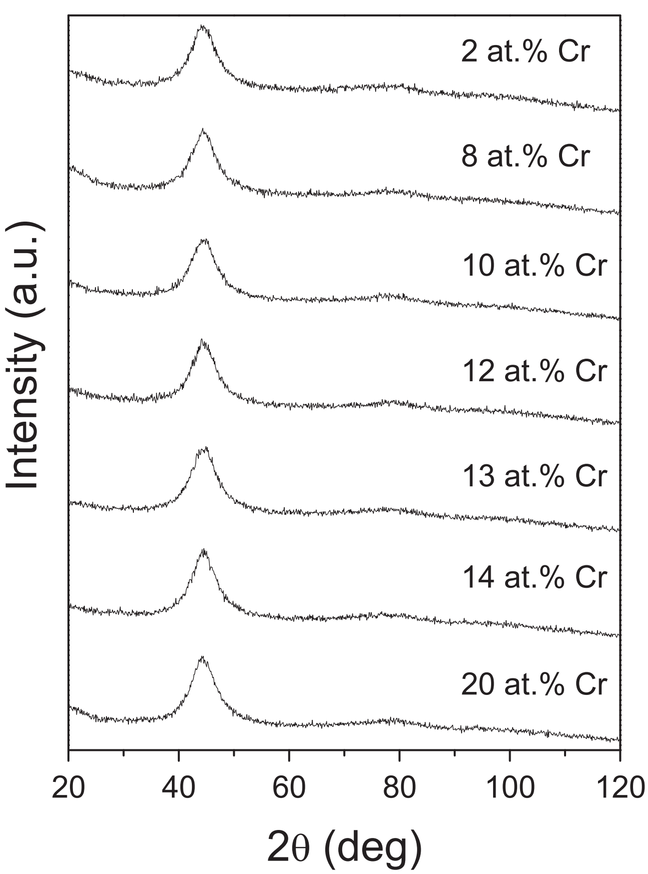

Fig. 1. XRD patterns of the as-quenched Cr-containing Vitroperm alloys.

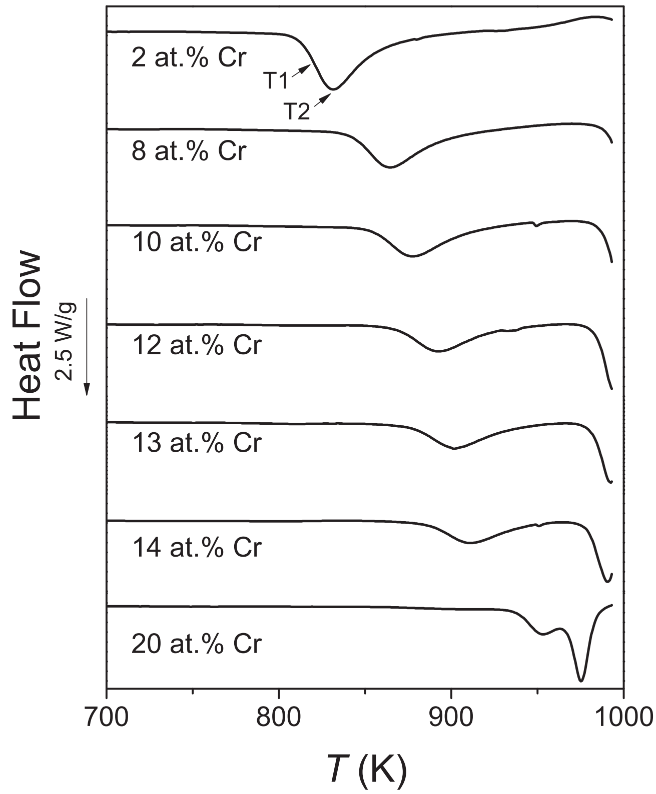

Fig. 2. DSC scans of the as-quenched Cr-containing Vitroperm alloys.

thermal stability, Fig. 2 shows the DSC scans of the as-quenched amorphous ribbons. From these scans up to 993 K at 20 K/min, two transformation processes can be observed, although the high temperature one shifts out of the explored range as the Cr content decreases. The first process corresponds to the crystallization of the bcc-Fe nanophase (α-Fe), as confirmed by XRD experiments. The increase of Cr content shifts the nanocrystallization peak to higher temperatures, stabilizing the amorphous structure. For the sample with 20 at% Cr, the primary crystallization peak overlaps with high temperature processes and the nanocrystalline state is not observed.

Magnetic entropy change curves were calculated using the software previously mentioned using a numerical approximation to the Maxwell equation. Fig. 3 shows the specific magnetization, $\sigma(T)$, at 200 Oe (upper panel) and $\Delta S_M(T)$ for a magnetic field change of 15 kOe (lower panel) for the amorphous ribbons. From $\sigma(T)$ data it can be observed that the Curie temperature of the amorphous alloys decreases as Cr content increases. This variation follows a linear dependence with a slope of -25.6 ± 0.8 K/at% of Cr, in agreement with previous studies [16]. Although the increase in Cr content allows us to reduce T_C, it is at the expense of a decrease of the magnetic entropy change peak (ΔS_M^{peak}) (Fig. 4). The refrigerant capacity (RC), calculated as the product of ΔS_M^{peak} times the full width half maximum (FWHM), also decreases with the increase of Cr content, although the variation is less significant than for ΔS_M^{peak} (comparing samples with 2 and 14 at% of Cr, the variation of the ΔS_M^{peak} is about 56%, while for RC it is 18%). For the sample with 20 at% Cr, RC cannot be calculated because the FWHM is out of the cryostat range. Both variations of ΔS_M^{peak} and RC are explained by the reduction of magnetic moment with the increase of Cr content in Vitroperm alloys following a dilution law [17,18], as can be observed in inset of Fig. 5. In fact, a linear evolution between ΔS_M^{peak} and the magnetic moment in Fe atoms (μ_{Fe}) can be