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The crystallization and properties of alloys with Fe partly substituted by Cr and Cu fully substituted by Au in Finemet

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Abstract

The structure, crystallization and magnetic properties of ribbons obtained by first making amorphous ribbons and then objecting them to a crystallization annealing have been published elsewhere by us previously. In the present work the soft magnetic ribbons $Fe_{73.5-x}Cr_xSi_{13.5}B_9Nb_3Au_1$ (numbers indicate at.%, $x = 1$–5) are prepared by fast quenching on a single copper wheel. X-ray diffraction patterns show that the as-cast samples are amorphous. Differential scanning calorimetry analysis indicates that the crystallization temperature of the α-Fe(Si) phase is a little higher than that of pure Finemet. With the same annealing conditions, the crystallization volume fraction decreases with increasing Cr content substituted for Fe. Hysteresis loops of as-cast samples measured by Permagraph show that domain walls are pinned. After appropriate annealing, the ultrasoft magnetic properties of nanocomposite materials are established. The magnetic entropy change, $|\Delta S_m|$, of studied samples has been determined, and a giant magnetocaloric effect is found. Our materials could be considered as promising magnetic refrigerants working at high temperatures (several hundreds °C).

Keywords: Nanocrystalline alloy; Soft magnetic amorphous system; Magnetocaloric effect

1. Introduction

The excellent soft magnetic properties of Finemet $Fe_{73.5}Si_{13.5}B_9Nb_3Cu_1$ (numbers indicate at.%) are directly correlated to its ultrafine structure composed of bcc-Fe rich crystals of nanometer size surrounded by a residual amorphous matrix [1,2]. This magnetic softening is mainly ascribed to the averaging out of magnetocrystalline anisotropy via ferromagnetic interaction between two constituent magnetic phases, and is reinforced by the negligible magneto elastic contribution due to desirable reduction of both internal quenched stresses as well as effective magnetostriction.

Recent studies have been devoted to investigate the substitution effect of P for B [3], Ag for Cu [4], Au for Cu [5] in Finemet, Co for Fe [6,7], Cr for Fe [8,9] as well as of Mn for Fe [10] on the structural, crystallization and magnetic properties of these alloys. When Cu substituted by Ag, there is very sharp exothermal peak exhibited in differential scanning calorimetry (DSC) [4], also the crystallization temperature of α-Fe(Si) phase as well as crystallization activation energy showed to be higher than those of pure Finemet. If Au is substituted for Cu, the crystallization temperature of the bcc-Fe(Si) phase is a little higher but crystallization activation energy is found to be less than that of pure Finemet. If Co is substituted for Fe, saturation magnetization, M_s, Curie temperature of amorphous state, T_C, showed to be higher than those of pure Finemet [6,7] but if Cr is substituted for Fe, T_C is drastically decreased [8,9].

The aim of this work is to present our study of the inclusion effect of Cr and Au on crystallization and properties of Finemet-type alloys.

2. Experiment

Amorphous ribbons with nominal compositions $Fe_{73.5-x}Cr_xSi_{13.5}B_9Nb_3Au_1$ ($x = 1$–5) have been prepared by rapid quenching on a copper wheel. The ribbons are 14.3–17 μm thick and 8 mm wide. The structure of samples was examined by X-ray diffraction (XRD; D 5005, Bruker) with Cu Kα radiation. The evolution of crystallization process was studied on differential scanning calorimetry (SDT 2900, TA Instruments). The

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ribbons were annealed in vacuum. Thermomagnetic curves were measured by a vibrating sample magnetometer (VSM-DMS 880, Digital Measurement Systems). Hysteresis loop parameters were carried out using automatic magnetic hysteresis graph (AMH-401A, Walker).

3. Results and discussion

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

DSC measurement on amorphous ribbons was performed in Ar atmosphere and Fig. 1 presents these results. There are clearly two separated exothermal peaks T_{p1} and T_{p2} on DSC curves, ascribed to the precipitation of bcc-Fe(Si) and boride phase, respectively. The first peak T_{p1} is ranging from 564 to 579 °C depending on the Cr content substituted for Fe, it is a little higher than that of pure Finemet [7] and of Finemet with Cu substituted by Au [5]. From Fig. 1 we can see also that the second peak T_{p2} exhibited with high sharpness relating to strong crystallization of boride phase. These results are fully agree with those reported in [9]. Fig. 2 presents the linear dependence of crystallization

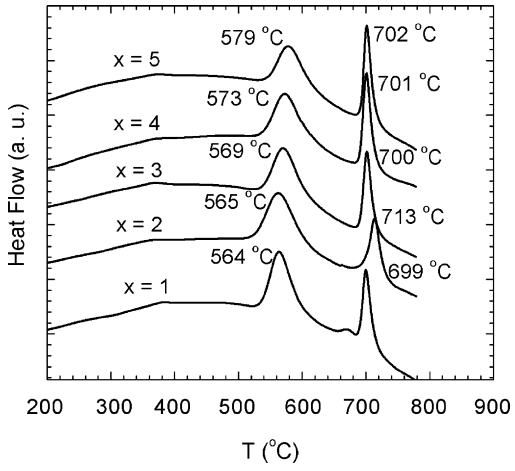

Fig. 1. DSC curves of as-cast ribbons $Fe_{73.5-x}Cr_xSi_{13.5}B_9Nb_3Au_1$ ($x = 1$–5) with heating rate of 20 K/min.

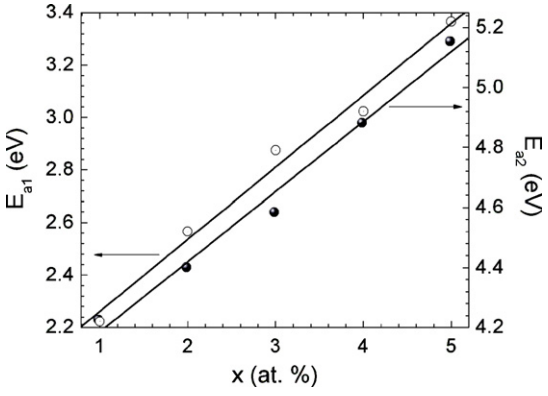

Fig. 2. Dependence of crystallization activation energies at the first peak E_{a1} and the second peak E_{a2} on Cr concentration.

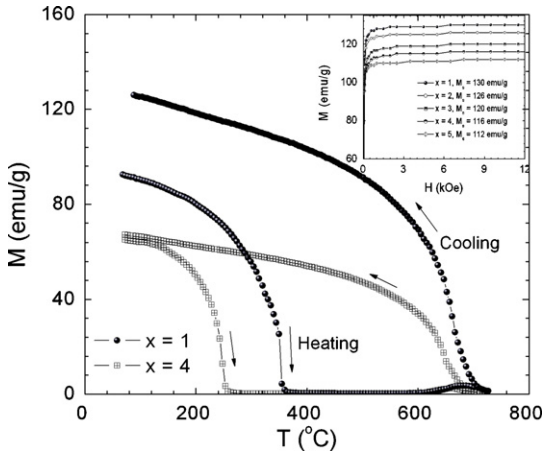

Fig. 3. Thermomagnetic curves of the samples $x = 1$ and $x = 4$ measured in magnetic field of 50 Oe.

activation energy of α-Fe(Si) phase (E_{a1}) and of boride phase (E_{a2}) on Cr content.

Crystallization kinetics of samples could be studied by measurements of thermomagnetic curves at low field. Fig. 3 shows the results for samples $x = 1$ and $x = 4$. We can see from this figure that at Curie temperature, T_C, of amorphous phase, magnetization suddenly decreases then material is in superparamagnetic state up to temperature region starting to crystallize. Magnetization curves measured along cooling cycle showing that the samples are of single phase in contrary with that of Ag substituted for Cu [4]. Insert of this figure is the magnetization curves of studied samples. The drastic decrease of T_C and M_s could be explained by ferromagnetic dilution due to Cr substitution for Fe as also observed in [8,9].

To promote the characteristic nanocrystalline structure, the samples were submitted to isothermal annealing in vacuum for 45 min. The DSC apparatus has been used to estimate the crystallized volume fraction (χ_f) of α-Fe(Si) phase [8] and the results showed that at the same annealing conditions χ_f decreases with increasing Cr content substituted for Fe which confirming that Cr atoms enhances crystallization temperature as observed from Fig. 1 and it could be associated with atomic rearrangements within the amorphous and FeCr phase which give rise to the formation of bcc-Fe(Si) nanograins, which coexist with the FeCr nanograins as assumed in [11].

Fig. 4 shows the XRD patterns of studied samples annealed at 550 °C for $t_a = 45$ min. The mean crystalline size (d_g) of α-Fe(Si) phase determined by XRD peak broadening analysis, using the Scherrer expression, is also indicated in Fig. 4. d_g decreased from 11.7 nm for sample $x = 1$ to 8.2 nm for sample $x = 5$ showing one again that Cr hinders crystallization.

Fig. 5 shows hysteresis loops of as-cast and annealed ribbon $x = 3$ ($T_a = 550$ °C, $t_a = 45$ min) measured at low magnetic field. Similar to that of $Fe_{73.5}Si_{13.5}B_9Nb_3Ag_1$ alloy [4] (but different for Finemet) the as-cast sample exhibits high rectangular coefficient of hysteresis loop. We suppose as in [8] that the FeCr nanograins, present in sample from as-cast state could act as wall pinning centers during magnetization process. As we see from this figure, after annealing, the soft magnetic properties