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Influence of cooling rate on the properties of $Fe_{73.5}Si_{13.5}B_9Nb_3Au_1$ ribbons

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Abstract. $Fe_{73.5}Si_{13.5}B_9Nb_3Au_1$ ribbons have been prepared by rapid cooling on a single copper wheel with different speeds of wheel of 10, 20, 30, and 40 m/s. The as-spun samples are amorphous. Upon annealing, the nanocrystalline phases are formed. Increasing the cooling rate leads to thinner ribbons, higher crystallization activation energy and crystallization volume fraction of the α-Fe(Si) phase, slightly increasing Curie temperature and soft magnetic properties of annealed ribbons. The large magnetic entropy change is observed for sample with v = 30 m/s. The mechanisms of the effects have been discussed.

1. Introduction

Recently, nanocrystalline soft magnetic materials attract significant interest both for fundamental research as well as production in moderately large scale. Among them, most attention is paid to nanocrystalline ferromagnet Finemet $Fe_{73.5}Si_{13.5}B_9Nb_3Cu_1$ which has been discovered by Yoshizawa and co-workers in 1988 at Hitachi Metals in Japan [1]. Nanocrystalline Fe-based alloys are almost magnetically isotropic due to ultrafine grain structure with average grain size less than 20 nm, e.g. less than domain width, therefore the movement of domain wall is not pinned at grain boundary [2]. When exchange interaction length is much larger than the average grain size, the macroscopic anisotropy averages out to given an effective anisotropy $<K>$ which is approximately three orders of magnitude smaller. In addition, it is considered that the negative saturation magnetostriction, λ_s, of the high Si nanocrystalline phase is closely counter balanced in volume terms by large positive λ_s for the glassy matrix so that the net λ_s is very small. These two factors contribute to the excellent soft magnetic properties of Fe-based nanocomposites.

In the previous papers, we have examined the influence of P substituted for B [3], Ag, Zn and Au for Cu [4-9], Co, Cr, Mn and Nb substituted for Fe in Finemet [10-16] on the crystallization, soft magnetic properties as well as giant magnetoimpedance of amorphous and nanocrystalline ribbons. Especially, at the first time in the world we have discovered the colossal magnetic effect in soft magnetic amorphous ribbons of Finemet-like alloy [17]. This behaviour has essential meaning in application of magnetic refrigeration.

In this report, we present the influence of speed of the wheel on the crystallization, magnetic properties and magnetocaloric effect of alloy $Fe_{73.5}Si_{13.5}B_9Nb_3Au_1$.

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2. Experiments

The amorphous ribbons $Fe_{73.5}Si_{13.5}B_9Nb_3Au_1$ with speeds of wheel of 10, 20, 30, 40 m/s have been obtained by rapid quenching technology on a single copper wheel. The structure analysis of as-cast ribbons is performed using X-ray diffractometer Bruker D5005 using Cu-K_α radiation. The thermal transitions are examined by SDT 2960 TA Instrument. The magnetic properties of the ribbon are measured by VSM DMS 880 and Permagraph AMH - 401A Walker. The thickness of ribbons is examined by Scanning Electron Microscope (SEM) 5410 LV, Jeol.

3. Results and discussion

We well known that when a liquid drop beat on the surface of the wheel, it will stretch on that a path before solidification and ejection from that and the higher speed of the wheel, the longer path. The increasing speed of the wheel make the thickness of ribbons thinner and the ratio between the area and volume of the ribbons that contact with the surface of the wheel is higher. This means that the wheel gets heat faster and more than from inside of the ribbon, so the ribbon is cooled faster. Therefore, the speed of the wheel is proportional to the cooling rate. It means that two concepts the speed of the wheel and the cooling rate are similar.

As we known, the cooling rate R is expressed by equation:

$$R = \frac{h(T_1 - T_0)}{C_p \rho t} \tag{1}$$

where T_1 is temperature of melting alloy, T_0 is temperature of wheel, h is heat transfer coefficient, C_p is thermal capacity, ρ is density, and t is thickness of ribbon. In our experiment, the T_1, T_0, C_p, ρ, h factors are always constant with the same composition of alloy. So, t is inversely proportional to R. The thicknesses of as-spun ribbons have been measured by SEM and the result shows that they are of 32.3, 30.9, 23.9, 19.3 μm for v =10, 20, 30, 40m/s, respectively.

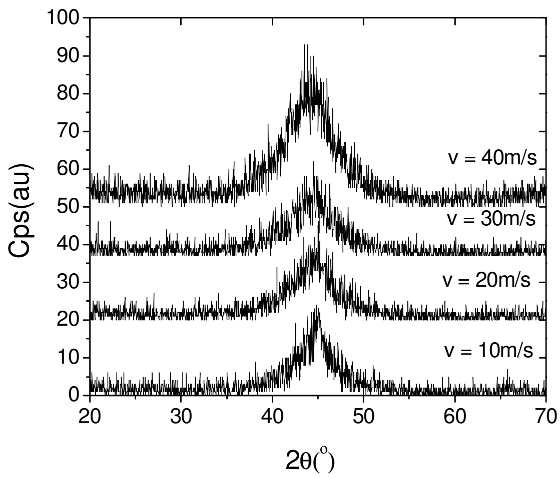


Fig. 1. X-ray diffraction patterns of as-spun ribbons $Fe_{73.5}Si_{13.5}B_9Nb_3Au_1$.

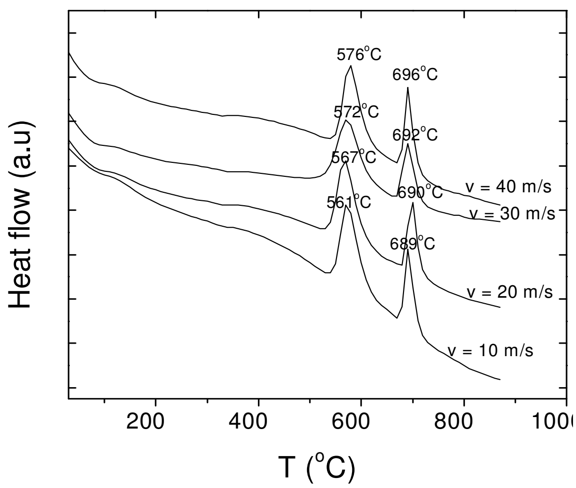
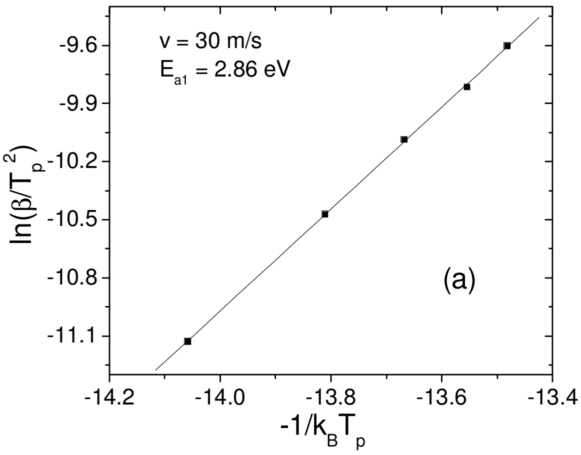


Fig. 2. DSC curves of the studied as-spun ribbons with heating rate of 20°C/min.

The X-ray diffraction patterns indicate that the as-spun ribbons are fully amorphous (see Fig. 1.). However, with the speed of the wheel of 10 m/s, the ribbon is tough and crisp. The others are soft and plastic.

The DSC curves of all as-spun samples measured in Ar atmosphere with heating rate of 20^{o}C/min. There are two exothermal peaks, the first peak corresponds to the crystallization of α-Fe(Si) phase and the second one is related to the forming of boride phase (Fig. 2). When increasing cooling rate, the first peak (T_{p1}) and the second one (T_{p2}) shift to high temperature. Namely, from 561 to 576^{o}C for first peak and from 689 to 696^{o}C for second one. With the high speed of the wheel, the system is in state of high disorder (near state of liquid of the system) and its entropy is maximum. Therefore, when changing to the crystallization state corresponding to the system have long-range order or its entropy is minimum, the difference on entropy between the rapid quenching state and the crystallization state is large, this leads to the crystallization peaks on the DSC curve shift to the higher temperature.



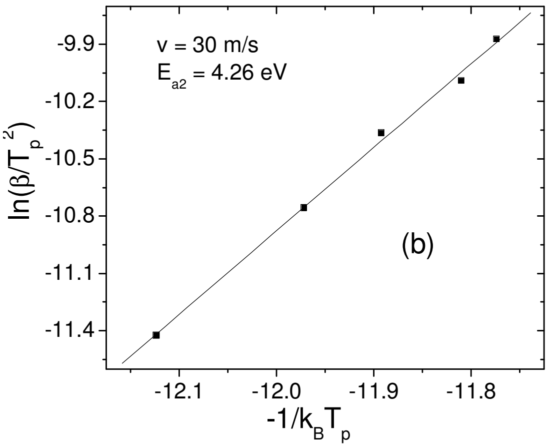


Fig. 3. Kissinger plot of sample v = 30 m/s, the first peak (a) and the second peak (b).

Tab. 1. The thickness, t, the crystallization activation energies, E_{a1} and E_{a2}, and the crystallization volume fraction, X_f, of the studied ribbons

Sample	t (μm)	T_{p1} (^{o}C)	T_{p2} (^{o}C)	E_1 (eV)	E_2 (eV)	X_f(540^{o}C-1h)
v = 10 m/s	32.2	561	689	2.53	3.59	60%
v = 20 m/s	30.9	567	690	2.85	4.03	78%
v = 30 m/s	23.9	572	692	2.86	4.26	84%
v = 40 m/s	19.3	576	696	2.96	4.35	85%

From the Kissinger's linear dependence, the crystallization activation energy E_{a1} of α-Fe(Si) phase and E_{a2} of boride phase are determined [18] (see Fig. 3 and Tab. 1). Increasing the cooling rate leads to increase both values of E_{a1} and E_{a2}. This is also similarly explained basing on the entropy difference between the rapid quenching state and the crystallization state in ribbon with different speed of the wheel.

The ribbons have been annealed in vacuum at temperature of 540^{o}C for 1 hour. From DSC curves of as-spun and annealed ribbons and using Leu and Chin expression:

$$X_f = \frac{\Delta H_1 - \Delta H_2}{\Delta H_1} \tag{2}$$

where X_f is the crystallization volume fraction of the α-Fe(Si) phase, ΔH_1, ΔH_2 are crystallization enthalpy of as-spun and annealed sample, respectively (see Fig. 4), we derive the crystallization volume fraction of the α-Fe(Si) phase. From Tab.1, we can see that the crystallization volume fraction increases when the cooling rate increases.

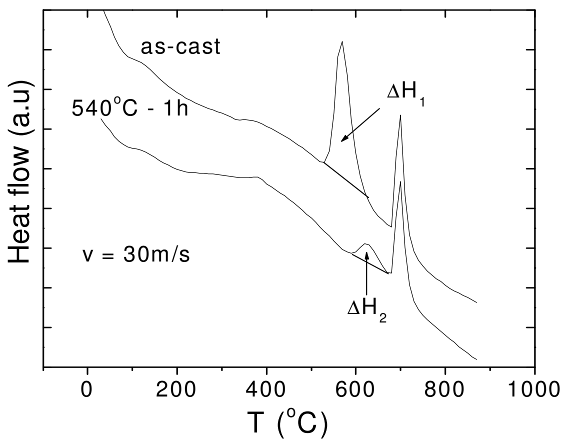


Fig. 4. DSC curves of as-spun and annealed ribbon with v of 30 m/s.

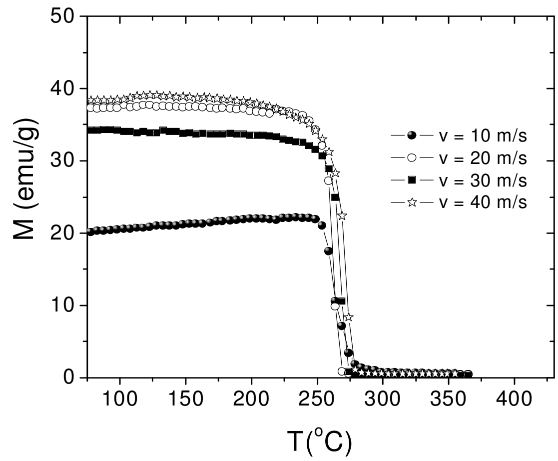


Fig. 5. Thermomagnetic curves of the studied samples measured in the field of 20 Oe .

All thermomagnetic curves measured in applied magnetic field of 20 Oe have similar shape (see Fig. 5). When the cooling rate increases, Curie temperature of amorphous phase (T_c) slightly increases (see Tab. 2). This can be explained as when the cooling rate rising, the inhomogeneity in structure of amorphous ribbons is high. As we well know, T_C of the ferromagnetic material depends on exchange interaction and coordination number. Exchange interaction depends on electron configuration and atom spacing. We assume that when raising the cooling rate, the deficiency of the atom position (vacancy) rises. This leads to the average distance of Fe atoms becomes larger and the exchange interaction is strengthened. It is the reason of increasing T_C of the ribbon when the speed of the wheel rises.

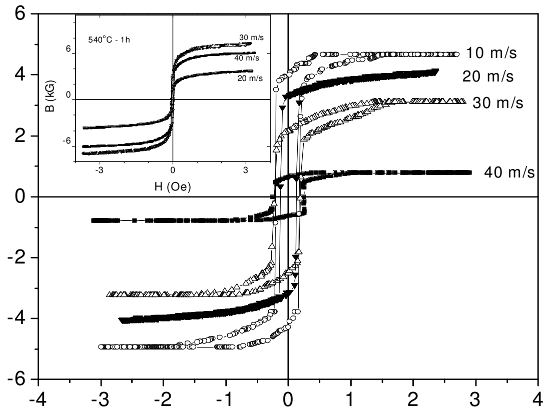


Fig. 6. Hysteresis loops of as-spun samples and samples annealed at 540°C for 1h (insert in Fig).

Hysteresis loops of as-spun and annealed ribbons have been measured (Fig. 6). The results show that coercivity (H_C) increases and saturation induction decreases when raising the cooling rate. It is noted that with higher cooling rate, the inhomogeneous in atom structure is higher and mechanical strain in the ribbons is higher, too (large elastic magnetic energy). This is the reason that hardens magnetization process and increases H_C. It can be assumed that in the ribbon only appeared the rotational process of domain wall (annealed ribbon) without the pinning displacement process of domain wall. This leads to magnetic saturation can be occurred in the low field and the hysteresis loops have rectangular shape. After annealing, soft magnetic properties of the studied nanocomposite samples are desirably improved (see Tab. 2). The change of μ_{max} and H_C is not monotone with cooling rate. At cooling rate of 30 m/s the soft magnetic properties are the best because the crystallization volume fraction is of 84% which possible leads to minimum magnetostriction.

Tab. 2. Curie temperature, T_c, and magnetic characteristics of as-spun and annealed ribbons

Sample	T_c (°C)	as-spun			annealed (540°C-1h)		
		B_r (kG)	μ_{max}	H_c (Oe)	B_r^* (kG)	μ_{max}	H_c (Oe)
v = 10 m/s	271	4.1	16,000	0.13			
v = 20 m/s	272	3.3	11,000	0.20	4.2	12,100	0.046
v = 30 m/s	273	2.4	4,600	0.21	3.4	25,000	0.034
v = 40 m/s	277	0.63	2,700	0.24	2.6	8,600	0.051

B_r^* is measured in the field of 3 Oe.

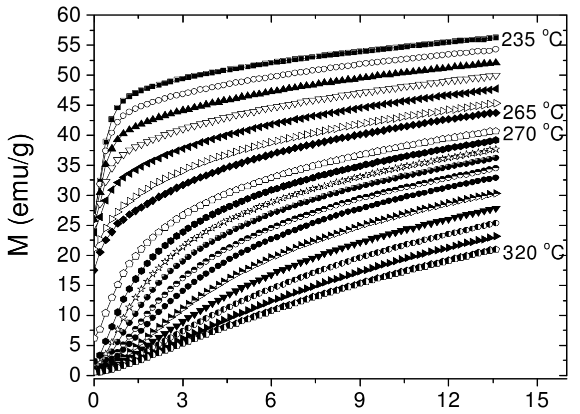


Fig. 7. Isothermal magnetization curves of sample with v of 30 m/s measured at different temperatures around T_C.

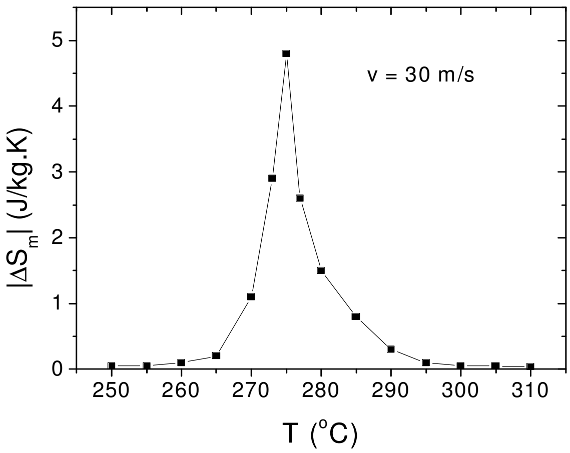


Fig. 8. Magnetic entropy change versus temperature in $Fe_{73.5}Si_{13.5}B_9Nb_3Au_1$ with v of 30 m/s in the field change ΔH = 1.35 T.

As we well known, the magnetic entropy change (ΔS_m) is correlated with the magnetization, the magnetic field strength by the fundamental Maxwell's relation [19]:

$$\Delta S_m(T,H) = \int_0^{H_{max}} \left(\frac{\partial M(T,H)}{\partial T} \right)_H dH = \frac{\partial}{\partial T} \left(\int_0^{H_{max}} M(T,H) dH \right) \tag{3}$$

where H_{max} is the final applied magnetic field.

In practice, the magnetic entropy change is intermittently calculated. Equation (3) shows that *M(T,H)dH* is area of M(H) curve. So Eq (3) is equal to:

$$\Delta S_m = \frac{S_2 - S_1}{T_2 - T_1} \tag{4}$$

where S_1 and S_2 are the area of M(H) curves at temperature T_1 and T_2, respectively.

From the isothermal magnetization curves (Fig. 7) and using Eq (5), the magnetocaloric effect of studied samples have been determined and the results show that the large magnetic entropy change ($|\Delta S_m|$) established at around respective Curie temperature of amorphous phase. Especially, with the speed of the wheel of 30m/s, the value of $|\Delta S_m|_{max}$ = 4.8 J/kg.K is obtained in magnetic field variation of 1.35 T (see Fig. 8). This value is larger than that of Gd [20] which was measured in field variation of 1.5 T. With another speeds of the wheel, the magnetocaloric effect is less. So the sample of 30 m/s can be considered as a good candidate with large magnetocaloric effect used in refrigeration technique at high temperature.

4. Conclusions

$Fe_{73.5}Si_{13.5}B_9Nb_3Au_1$ ribbons with the wheel speed of 10, 20, 30 and 40 m/s have been prepared in amorphous structure. The difference of the speed of the wheel has influenced on the crystallization, magnetic properties and magnetocaloric effect of the ribbons. The increase of cooling rate leads to increasing crystallization activation energy and crystallization volume fraction. Increasing the inhomogeneity in structure of as-spun ribbons when increase cooling rate that makes higher coercivity and Curie temperature of amophous phase. The maximum magnetic entropy change $|\Delta S_m|_{max}$ is quite large, the value of $|\Delta S_m|_{max}$ is 4.8 J/kg.K for 30m/s ribbon. The material can be used in refrigeration technique at high temperature.

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