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The effect of Zn, Ag and Au substitution for Cu in Finemet on the crystallization and magnetic properties

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Abstract

Soft magnetic ribbons of Finemet compound with Zn, Ag and Au substituted for Cu: $Fe_{73.5}Si_{13.5}B_9Nb_3Cu_{1-x}M_x$ (M = Zn, Ag, Au; $x = 0.5, 1.0$) have been fabricated by rapid quenching technique with wheel speeds of 10, 25 and 30 m/s, respectively. The crystallization evolution of samples examined by DSC measurements showed that the high cooling rates make the ribbons in amorphous state whereas the samples with M = Zn; $x = 0.5, 1.0$ showed to be partly crystallized when they fabricated by the wheel speed of 10 m/s. In the case of Zn ($x = 0.5, 1.0$) and Ag ($x = 1.0$) substitution there is a sharp peak in the DSC curve corresponding to crystallization of α-Fe(Si) phase. However, the role of Au is similar to that of Cu. Hysteresis loops of as-cast samples exhibited square form which relates to the pinning centers in domain wall displacement. After appropriate annealing, the ultrasoft magnetic properties of studied ribbons are obtained.

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Keywords: Nanocrystalline materials; Amorphous and glassy solid; Soft magnetic amorphous system

1. Introduction

The Finemet type of nanocomposite alloy, originally prepared at Hitachi Metals in Japan [1] with composition $Fe_{73.5}Si_{13.5}B_9Nb_3Cu_1$ (at%) is now well established commercially. It was prepared by melt spinning to have amorphous structure ribbon, which was then partially devitrified. In the optimum magnetic state, the alloy exhibited a two-phase nanocomposite structure and a very small volume fraction (~1%) of nanometer scale Cu particles (~5 nm). Cu particles act as nucleation sites for the Fe–Si crystallites during devitrification [2].

Yoshizawa et al. [3] reported that addition of Nb and Cu was required to obtain the nanocrystalline structure in Fe–Si–B based alloys. Thus the role of Nb and Cu in the nanocrystallization effect has been a great interest. HREM image showed that the remaining amorphous phase between the nano-particles was enriched by B and Nb and a small amount of Si [4]. In addition to these two major phases, a strongly Cu-enriched phase (~60% or higher) was observed with fcc structure. In the previous papers, we investigated the substitution effect of P for B [5], Co for Fe [6], Cr for Fe [7] and Ag for Cu [8] on the structure and properties of Finemet-type compounds.

In this report, we present our study on the substitution effect of $Fe_{73.5}Si_{13.5}B_9Nb_3Cu_{1-x}M_x$ alloys (M = Zn, Ag, Au; $x = 0.5, 1.0$) on their crystallization and magnetic properties.

2. Experimental

The soft magnetic ribbons $Fe_{73.5}Si_{13.5}B_9Nb_3Cu_{1-x}M_x$ (M = Zn, Ag, Au; $x = 0.5, 1.0$) have been prepared by rapid quenching technique on a single copper wheel. The linear speeds of wheel were $v = 10$ and 30 m/s which were applied for compositions M = Zn ($x = 0.5$ and 1.0); $v = 25$ m/s for M = Ag ($x = 0.5$ and 1.0); $v = 30$ m/s for composition M = Au, $x = 1.0$. The ribbons are of 8 mm wide and 16.8–50 μm thick.

The structure of the ribbons was examined by X-ray diffractometer D5005 Bruker. The thermal transition analysis was studied by SDT 2960 TA Instruments. The

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ribbons were annealed in vacuum. The microstructure of annealed samples was examined by scanning electron microscope (SEM) 5410 LV, Jeol. The thermomagnetic curves of as-cast ribbons were measured by vibrating sample magnetometer (VSM) DMS 880 Digital Measurement System and the magnetic properties of studied samples were determined by using Permagraph AMH-401 A, Walker.

3. Results and discussion

For the compositions $Fe_{73.5}Si_{13.5}B_9Nb_3Cu_{1-x}Zn_x$ ($v = 10$ m/s) it was shown that the as-cast samples partly crystallized with a small amount of α-Fe(Si). We suppose that only the surface of ribbons contacted with copper wheel was amorphous whereas the other surface of ribbons contacted with air and the part inside the ribbons are more or less crystallized (thickness of ribbons was about 50 μm). Increasing wheel speed to 30 m/s (ribbon thickness was about 25 μm) led to the formation of fully amorphous state in both samples $x = 0.5$ and 1.0. The XRD analysis showed that the rest as-cast samples $Fe_{73.5}Si_{13.5}B_9Nb_3Cu_{1-x}Ag_x$ ($x = 0.5$, 1.0) and $Fe_{73.5}Si_{13.5}B_9Nb_3Cu_{1-x}Au_1$ are also amorphous.

Fig. 1 presents the DSC patterns of as-cast samples $Fe_{73.5}Si_{13.5}B_9Nb_3Cu_{1-x}Zn_x$ ($x = 0.5$, 1.0) with wheel speeds of 10 and 30 m/s.

As we can see from this figure, the sample $x = 0.5$ prepared by low wheel speed was strongly crystallized because there is only a small exothermal peak occurring at 728 °C (Fig. 1a) relating to weak crystallization of remaining boride phase whereas this composition prepared by higher wheel speed clearly reveals with two crystalline phases (Fig. 1b): the first peak occurring at 559 °C relating to the crystallization of α-Fe(Si) phase and the second one at 702 °C corresponds to the crystallization of boride phase.

The crystallization evolution of sample $x = 1$ was quite different: with low wheel speed, there was only one sharp peak occurring at 607 °C in the DSC curve (Fig. 1a) and this α-Fe(Si) phase was performed in narrow temperature interval, around 50 °C which is higher than that of pure Finemet [6]. Because of the absence of the second peak in the DSC curve of ribbon $x = 1.0$, $v = 10$ m/s, it could be assumed that the boride phase was formed just in fabricated stage due to slower cooling rate. In higher cooled sample, the DSC scan exhibits two crystallized peaks (Fig. 1b), one at $T_{p1} = 602$ °C (α-Fe(Si) phase) and another at $T_{p2} = 751$ °C (boride phase). Both T_{p1} and T_{p2} here are higher than those of pure Finemet [6]. From the DSC analysis, it could be understood that although Zn

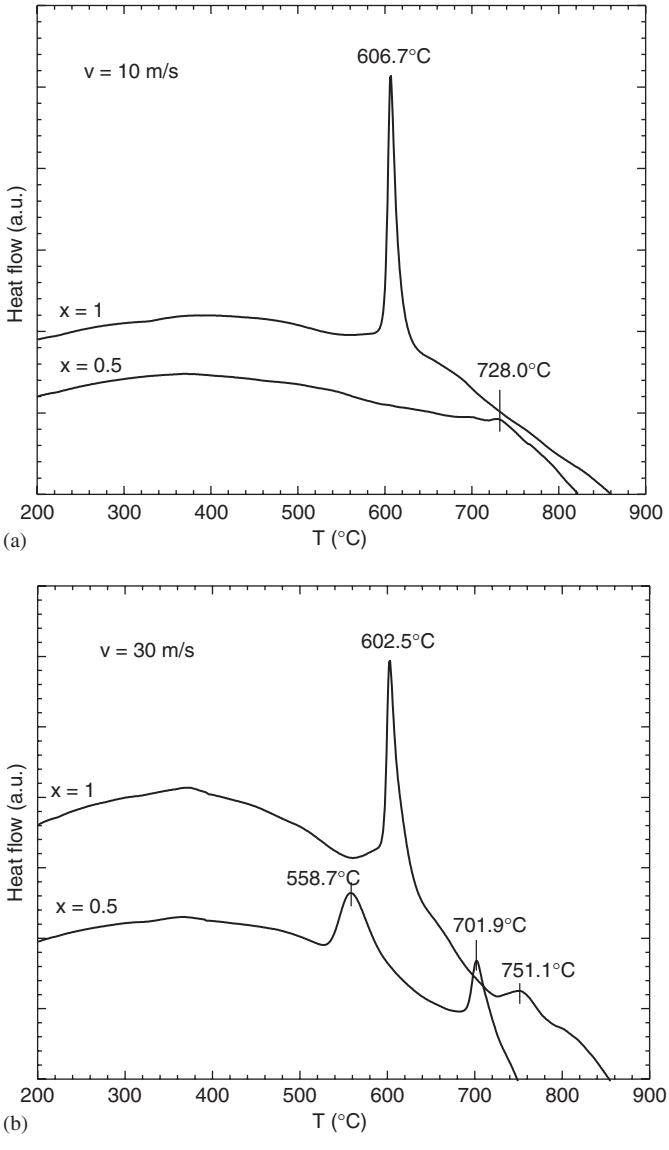

Fig. 1. DSC patterns of as-cast samples $Fe_{73.5}Si_{13.5}B_9Nb_3Cu_{1-x}Zn_x$ ($x = 0.5$, 1.0), (a) for ribbons with $v = 10$ m/s and (b) for ribbons with $v = 30$ m/s.

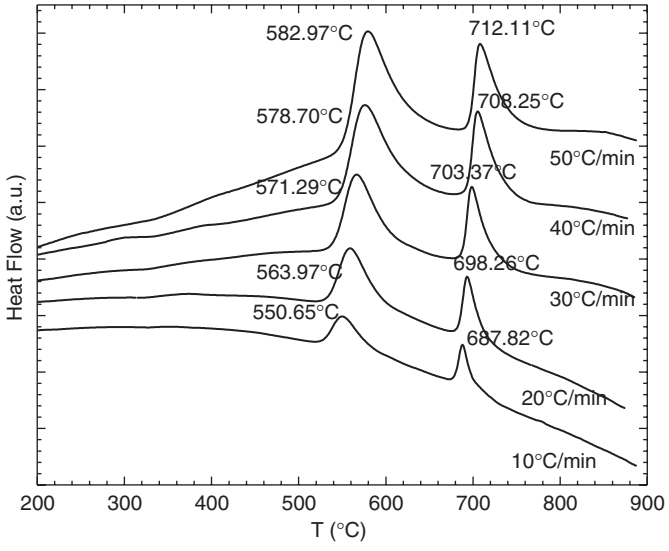

Fig. 2. DSC curves of as-cast ribbon $Fe_{73.5}Si_{13.5}B_9Nb_3Cu_{0.5}Ag_{0.5}$ measured with different heating rates.

with lower melting temperature, T_m ($T_m = 419.58\,^{\circ}C$) than that of Cu ($T_m = 1053.40\,^{\circ}C$), it is more difficult to create the crystallization nucleation for α-Fe(Si) phase. Furthermore when the crystallization started, it finished very fast similar to that published in the case of Ag fully substituted for Cu [8].

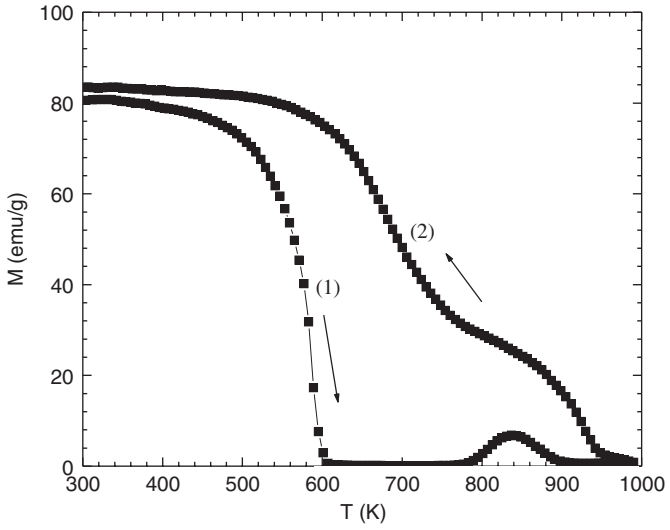

Fig. 3. Thermomagnetic curves of as-cast ribbon $Fe_{73.5}Si_{13.5}B_9Nb_3Cu_{0.5}Ag_{0.5}$ ($v = 25$ m/s), (1) heating cycle and (2) cooling cycle.

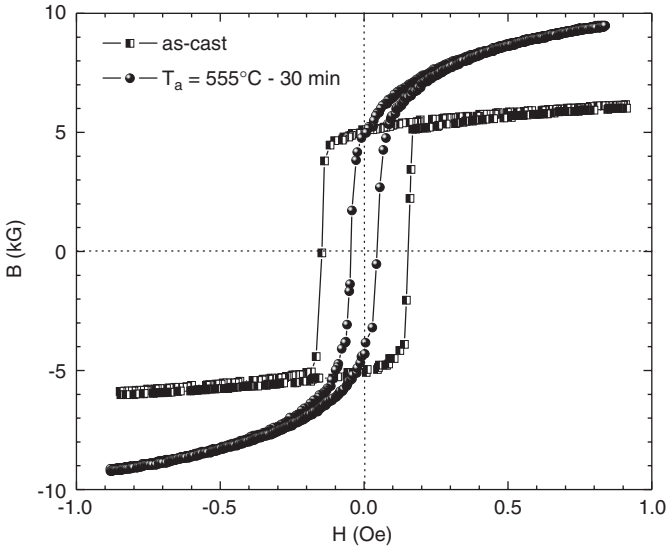

Fig. 4. The hysteresis loops of as-cast and annealed ribbons $Fe_{73.5}Si_{13.5}B_9Nb_3Cu_{0.5}Ag_{0.5}$.

Differently to the sample $Fe_{73.5}Si_{13.5}B_9Nb_3Ag_1$, in the sample with Ag partly substituted for Cu: $Fe_{73.5}Si_{13.5}B_9Nb_3Cu_{0.5}Ag_{0.5}$, the DSC curves (Fig. 2) exhibited two exothermal peaks T_{p1} and T_{p2} at temperature ranges which are a little higher than those of pure Finemet. The similar feature was observed for as-cast sample $Fe_{73.5}Si_{13.5}B_9Nb_3Au_1$, the T_{p1} (547–579 °C) and T_{p2} (687–714 °C) peaks occurred at temperatures only a little higher than those for pure Finemet with the same shape of DSC curve.

The crystallization kinetics of the studied ribbons could be observed by measurement of the thermomagnetic curves. Fig. 3 presents the $M(T)$ curves of the ribbon $Fe_{73.5}Si_{13.5}B_9Nb_3Cu_{0.5}Ag_{0.5}$ (wheel speed of 25 m/s) measured in magnetic field of 50 Oe.

One can see from Fig. 3 that when the temperature increases, magnetization M suddenly decreases at Curie temperature, T_C, of amorphous phase. With further increasing temperature, the ribbon is in the superparamagnetic up to the region starting to crystallize the α-Fe(Si) phase which makes increasing magnetization, then M decreases at T_C of the composite sample. On returning from high temperature, a large amount of α-Fe(Si) grains as well as boride $Fe_{2,3}B$ grains is crystallized leading to an increase of magnetization below T_C of material. The $M(T)$ curve measured along the cooling cycle shows that there is multi-phase structure occurring in the ribbons. The similar picture has been obtained also for the rest samples. Beside that, the thermomagnetic curves of $Fe_{73.5}Si_{13.5}B_9Nb_3Au_1$ sample exhibits a smooth shape like in the case of Finemet compound that indicated the main phases in Finemet of Cu and Au are α-Fe(Si), remaining amorphous phase and the clusters of Cu or Au located at grain boundary.

All as-cast ribbons exhibit pinning of domain wall displacement (Fig. 4) while in annealed ribbons, the ultrasoft magnetic properties have been achieved (see Fig. 4 and Table 1).

Optimum annealing temperature, T_a, was not identified for different samples. The SEM pictures and XRD patterns of annealed ribbons showed that the grains have the size in the range of 12–20 nm.

Table 1
Magnetic characteristics of several studied samples

Sample		μ_0	μ_{max}	H_c (Oe)
$Fe_{73.5}Si_{13.5}B_9Nb_3Cu_{0.5}Zn_{0.5}$	$v = 30$ m/s, as-cast	615	910	0.33
	$v = 30$ m/s, $T_a = 530\,^{\circ}C$—30 min	11,000	24,100	0.06
$Fe_{73.5}Si_{13.5}B_9Nb_3Cu_{0.5}Ag_{0.5}$	$v = 25$ m/s, as-cast	10,000	35,000	0.15
	$v = 30$ m/s, $T_a = 555\,^{\circ}C$—30 min	25,000	70,000	0.046
$Fe_{73.5}Si_{13.5}B_9Nb_3Au_1$	$v = 30$ m/s, as-cast	1300	6900	0.144
	$v = 30$ m/s, $T_a = 530\,^{\circ}C$—90 min	19,000	99,000	0.022

4. Conclusions

(i) The $Fe_{73.5}Si_{13.5}B_9Nb_3Cu_{1-x}M_x$ (M = Zn, Ag, Au; $x = 0.5$, 1.0) ribbons have been prepared in amorphous structure with wheel speed $v \geqslant 25$ m/s.

(ii) In the samples with Zn and Ag fully substituted for Cu, the crystallization of α-Fe(Si) phase occurred at temperatures higher than that of pure Finemet and exothermal peaks exhibited with high sharpness whereas the role of Au in the crystallization is similar to that of Cu.

(iii) There is multi-phase structure in the $M(T)$ curves measured in cooling cycle for samples with Zn and Ag doping.

(iv) After appropriate annealing, the ultrasoft magnetic properties of studied samples are established.

Acknowledgments

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