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CRYSTALLIZATION BEHAVIOUR OF Fe-(Nb,Cu)-Si-B METALLIC GLASSES

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Abstract

The crystallization behaviour and Curie temperatures of Fe-(Nb,Cu)-Si-B metallic glasses were studied by means of differential scanning calorimetry (DSC), thermomagnetic gravimetry (TMG) and X-ray diffraction. The agreement between the DSC and TMG results was complete. For all Fe–Si–B amorphous alloys, two-peak crystallization was observed with the primary crystallization of α-Fe(Si) followed by eutectic crystallisation. The effects of Cu and Nb additions on the crystallization behaviour and on the activation energies for each stage of the crystallization process of Fe–Si–B glass were investigated.

Keywords: crystallization, Fe-(Nb,Cu)-Si-B metallic glasses

Introduction

Amorphous Fe–Si–B alloys are known to exhibit excellent soft magnetic properties, which make them attractive for many applications, such as transformer cores and high-frequency applications. Yoshisava *et al.* [1] developed new nanocrystalline Fe-(Nb,Cu)-Si-B alloys, denoted FINEMET, whose soft magnetic properties in many cases exceed those of amorphous materials. The source of FINEMET is an Fe–Si–B-based amorphous alloy, containing a small amount of Cu and Nb, prepared by rapid solidification (melt-spinning). Annealing of the ribbon between 750 and 850 K creates a very fine structure with a typical grain diameter of 10–20 nm. The most studied of these nanocrystalline materials is the alloy with nominal composition $Fe_{73.5}Cu_1Nb_3Si_{13.5}B_9$ [2–7].

In the crystallization of these amorphous alloys, Cu is thought to enhance the nucleation of α-Fe(Si) crystals (Cu atoms act as nucleation-centres), while Nb hinders their growth. As a result, a structure of α-Fe(Si) nanocrystals, develops, embedded in an amorphous residual phase in the form of grain boundaries [4].

A knowledge of the dependence of the thermal stability and crystallization kinetics of Fe–Si–B glasses on composition is of considerable importance for their high-frequency applications, and has been the subject of numerous studies [8, 9].

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In the present paper, we report results on the Curie points, thermal stabilities and crystallization behaviour of Fe–Si–B glasses with different compositions and of Fe–Cu, Nb–Si–B amorphous alloys with different additions of Cu and Nb. Measurements of the kinetics of crystallization of all glasses studied by means of differential scanning calorimetry (DSC) and thermomagnetic gravimetry (TMG) are also presented.

Experimental

Amorphous Fe-(Cu,Nb)-Si-B ribbons 30 μm thick and 2–3 mm wide were produced by melt-spinning on laboratory equipment (onto a copper wheel with cooling rates of about 1.10^5 deg·s^{-1}).

The amorphous character of the as-quenched ribbons was checked by X-ray diffraction and DSC. DSC under isothermal and isochronal conditions was performed with a Perkin-Elmer DSC-2C with a temperature accuracy of 0.5 deg, in an argon atmosphere.

TMG was carried out with a Perkin-Elmer TGS-2 thermobalance in an argon stream by Faraday's method [10]. For these experiments, the external magnetic field of a small magnet was applied to the sample and the temperature variation of the magnetic force (M_s) was recorded as the apparent change in mass of the sample.

Table 1 Curie (T_c) and crystallization (T_x, T_{max1}, T_{max2}) temperatures, crystallization enthalpy (ΔH_{cr}) and activation energy for crystallization (Q) of Fe-(Cu, Nb)-Si-B glasses studied

Composition/	T_x/	T_{max1} /	T_{max2} /	T_c /	ΔH_{cr} /	Q /kJ·mol^{-1}	
at.%	K				J·g^{-1}	I peak	II peak
$Fe_{78}Si_6B_{16}$	811.8	817.0	831.5	651	155	434	382
$Fe_{78}Si_9B_{13}$	821.5	829.8	845.0	662	142	358	315
$Fe_{78}Si_{10}B_{12}$	814.0	822.3	841.3	661	134	383	350
$Fe_{78}Si_{13}B_9$	806.5	815.6	845.0	660	117	304	268
$Fe_{77}Cu_1Si_{13}B_9$	748.1	756.2	831.9	–	117	230	251
$Fe_{77}Nb_1Si_{13}B_9$	847.4	852.0	–	–	88	387	–
$Fe_{75}Nb_3Si_{13}B_9$	881.9	889.4	–	599	48	369	–
$Fe_{73.5}Cu_1Nb_3Si_{13.5}B_9$	814.3	832.6	–	603	46	342	–

Results and discussion

The compositions of the amorphous alloys studied are presented in Table 1.

DSC measurements on the as-quenched Fe-(Cu,Nb)-Si-B samples, carried out under scanning conditions ($V=dT/dt=20$ deg·min^{-1}), are reported in Fig. 1 and 2. All Fe–Si–B glasses exhibit two overlapping crystallization peaks

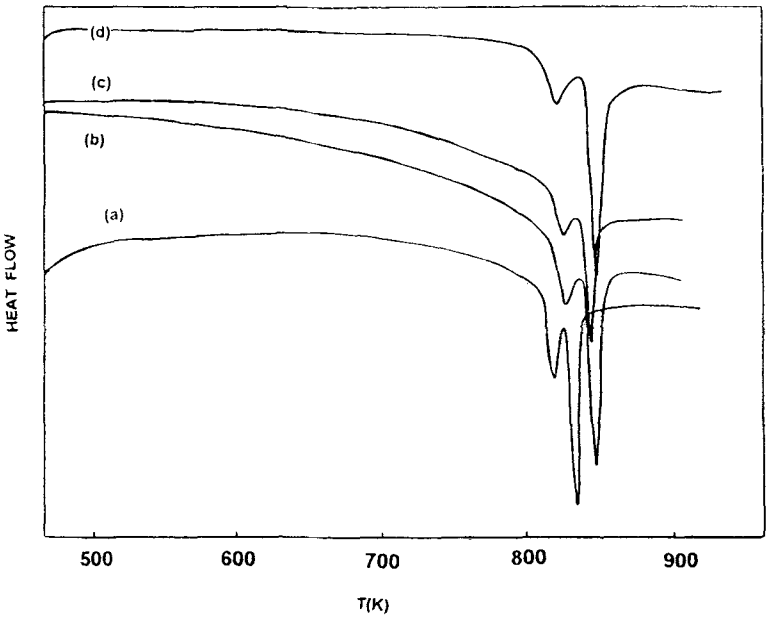

Fig. 1 DSC records for Fe–Si–B alloys studied: (a) $Fe_{78}Si_6B_{16}$, (b) $Fe_{78}Si_9B_{13}$, (c) $Fe_{78}Si_{10}B_{12}$ and (d) $Fe_{78}Si_{13}B_9$, at a heating rate of 20 deg·min^{-1}

(Fig. 1), with crystallization enthalpies ΔH_{cr} for the overall process of about 125 J/g.

The temperature of onset of crystallization, T_x, and the peak temperatures of the first and second crystallization reactions, T_{max1} and T_{max2}, measured at a heating rate of 20 deg·min^{-1}, are reported in Table 1, where the composition dependence of these temperatures can be seen.

It is clear from Table 1 that, while T_{max2} is rather insensitive to variation of the Si content, T_x and T_{max1} decrease on moving away from the eutectic composition. Surinach *et al.* [9] found the same maximum in T_x, T_{max1} and T_{max2} at around 8 at.% Si measured at a heating rate of 80 deg·min^{-1}.

The addition of 1 at.% Cu ($Fe_{77}Cu_1Si_{13}B_9$) leads to a significant decrease in the thermal stability (T_x decrease), as a result of which the temperature interval between the two crystallization stages increases (Fig. 2a). Fe–Si–B amorphous alloys containing Nb display a single crystallization peak, with $\Delta H_{cr}=88$ J/g (Fig. 2b). The crystallization and peak temperatures of Fe-(Cu,Nb)-Si-B amorphous alloys are also listed in Table 1. It can be seen that Nb leads to increase in T_x and T_{max}. The alloy $Fe_{73.5}Cu_1Nb_3Si_{13.5}B_9$ also gives a single exothermal peak at 814 K, and a second high-temperature effect (at about 1000 K). DSC traces of a sample heated at 20 deg·min^{-1} are shown in Fig. 2d. The exothermal effect at 814 K is due to the formation of a bcc Fe solid solution and an Fe_3Si phase with an enthalpy variation ΔH_{cr} of 46 J/g. At higher temperatures, a sec-

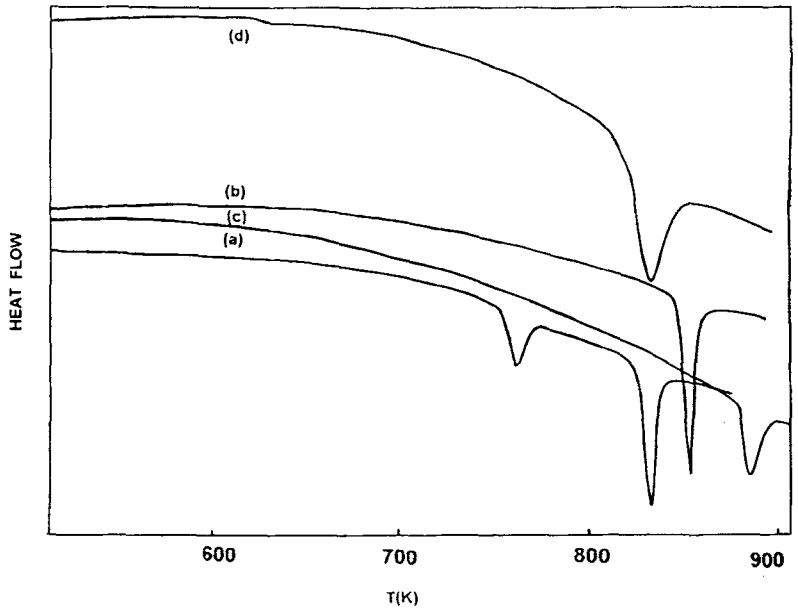

Fig. 2 DSC records for Fe-(Cu,Nb)-Si-B alloys studied: (a) $Fe_{77}Nb_1Si_{13}B_9$, (b) $Fe_{77}Cu_1Si_{13}B_9$, (c) $Fe_{75}Nb_3Si_{13}B_9$ and (d) $Fe_{73.5}Cu_1Nb_3Si_{13.5}B_9$, at a heating rate of 20 deg·min^{-1}

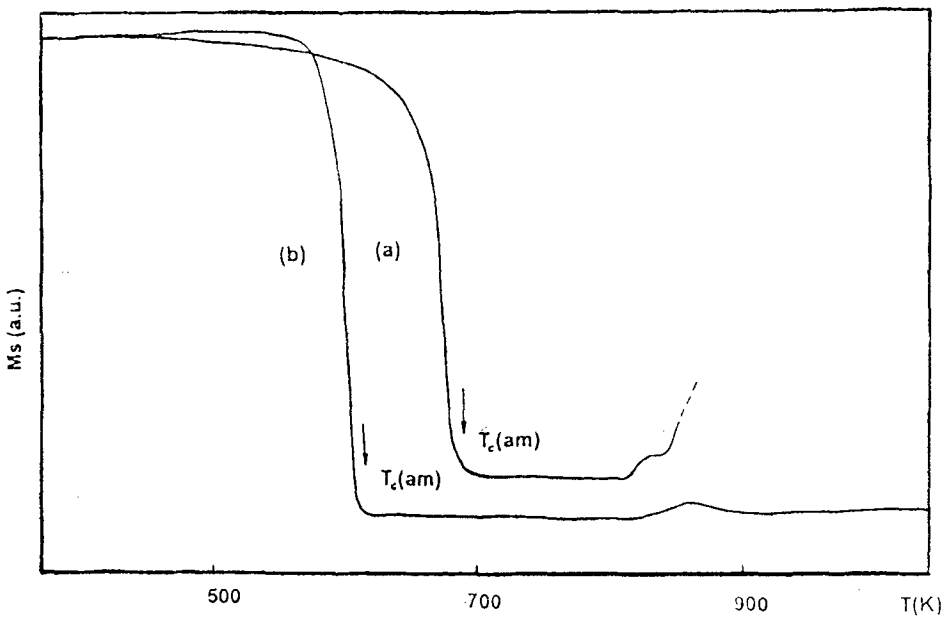

Fig. 3 TMG curves of (a) $Fe_{78}Si_{13}B_9$ and (b) $Fe_{73.5}Cu_1Nb_3Si_{13.5}B_9$ at a heating rate of 20 deg·min^{-1}

ond peak is associated with the formation of boride phases. The DSC temperature limit does not allow the accurate determination of T_x and ΔH_{cr} for this transformation.

TMG records of the as-quenched alloys (Fig. 3) clearly indicate the Curie temperatures, T_c of the amorphous alloys and also the crystallization temperatures, in full agreement with the results of DSC analysis. The crystallization onset is evidenced as an increase in the magnetic force M_s (apparent weight), relating to the formation of magnetic crystalline phases.

The Curie temperatures T_c of the Fe–Si–B amorphous alloys studied (Table 1) are rather insensitive to variations of the Si content, provided that the Fe content remains constant, but T_c decreases on addition of Nb.

X-ray studies confirmed that the first crystallization reaction of Fe–Si–B glasses is mainly due to the formation of bcc α-Fe(Si) crystals. This is in agreement with our DSC and TMG results and with TEM observations [8, 9, 11, 12] on the same amorphous alloys. During the second transformation stage (second exotherm), a tetragonal Fe_3B phase crystallizes. After heat treatment of $Fe_{73.5}Cu_1Nb_3Si_{13.5}B_9$ in DSC at 814 K, a crystalline peak corresponding to a bcc Fe solid solution and an Fe_3Si phase is observed. Heating up to 1000 K produces a mixture of boride phases.

To obtain information about the activation energies of the crystallization reactions, DSC studies at heating rates varying between 20 and 80 deg·min^{-1} were performed on all alloys investigated.

Figure 4 shows the dependence of the temperature of the maximum in the DSC curve, T_{max}, on the heating rate $V=dT/dt$ in Kissinger coordinates [13]. From the slope of the straight line obtained, Kissinger activation energies Q

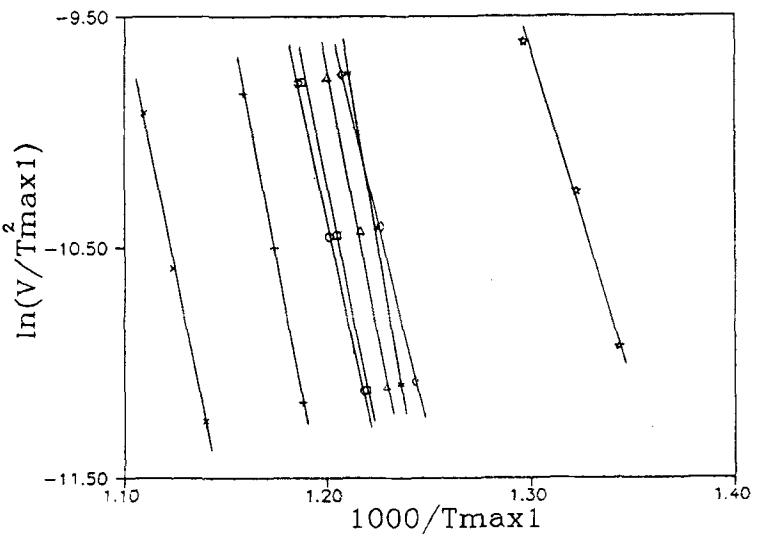

Fig. 4a Kissinger plots for first crystallization stage of Fe-(Cu,Nb)-Si-B alloys studied

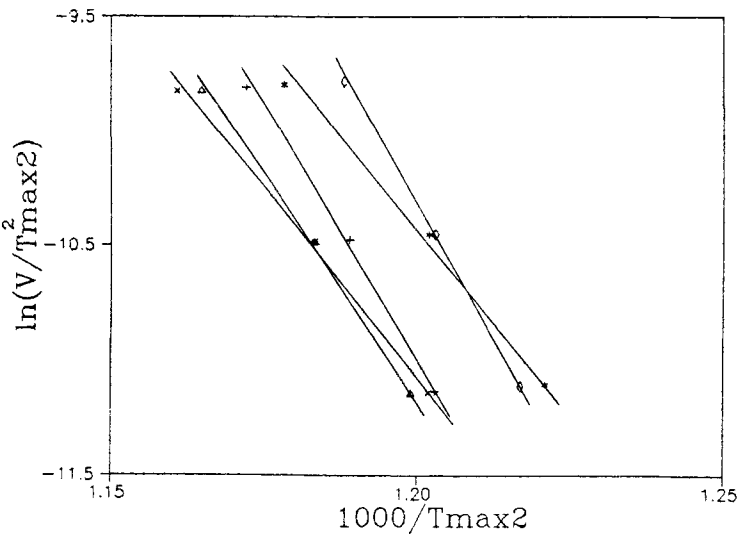

Fig. 4b Kissinger plots for second crystallization stage of Fe-(Cu,Nb)-Si-B alloys studied

were determined; they are listed in Table 1. In all cases for Fe–Si–B glasses, the activation energy of the second crystallization peak is lower than that of the first one [9], indicating an increase in the driving force for the second crystallization reaction. Both activation energies increase slightly on moving away from the eutectic composition. Copper decreases the activation energy of the first reaction only; at the same time, Q for the second reaction remains unchanged. Fe–Nb–Si–B alloys (with one crystallization peak) have higher Q of about 375 kJ·mol^{-1}; on increase of the Nb content, Q also increases slightly. Addition of 1 at.% Cu to Fe–Nb–Si–B leads to a lower Q. The activation energy for the formation of a bcc Fe solid solution in $Fe_{73.5}Cu_1Nb_3Si_{13.5}B_9$ (350 kJ·mol^{-1}) is comparable with those determined by means of electrical resistivity measurements on alloys with the same nominal composition [3].

Conclusions

The crystallization behaviour of Fe-(Nb,Cu)-Si-B amorphous ribbons produced by melt-spinning has been studied by means of X-ray, DSC and TMG. The transformation of the Fe–Si–B amorphous alloy exhibits two stages, evidenced as a double-peaked DSC exotherm. In the first, the α-Fe(Si) phase is formed. During the second stage, eutectic crystallization occurs. The annealed Fe–Nb–Cu–Si–B alloy consists of a mixture of nanocrystalline grains of bcc Fe solid solution and amorphous regions. The presence of Cu leads to separation of the two overlapping crystallization peaks, mainly through a decrease in onset of the first exothermic effect, probably because Cu has a tendency to segregate from Fe and has an effect on the nucleation.

The activation energy for each crystallization stage was determined at all the compositions studied, using Kissinger formalism.

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Zusammenfassung — Mittels Differential-Scanningkalorimetrie (DSC), thermomagnetischer Gravimetrie (TMG) und Röntgendiffraktion wurde das Kristallisationsverhalten und die Curie-Punkte der metallischen Gläser Fe-(Nb,Cu)-Si-B untersucht. Zwischen DSC- und TMG-Ergebnissen besteht volle Übereinstimmung. Bei allen amorphen Fe–Si–B-Legierungen wurden zwei Peaks Kristallisation beobachtet, wobei die primäre Kristallisation von α-Fe(Si) von einer eutektischen Kristallisation gefolgt wird. Der Einfluß des Zusatzes von Cu und Nb auf das Kristallisationsverhalten und auf die Aktivierungsenergien für jede einzelne Stufe des Kristallisationsprozesses von Fe–Si–B-Gläsern wird untersucht.