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Influence of Ag admixtures on the crystallization of amorphous $Fe_{75}Si_9B_{16}$

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This work studies the influence of the Ag admixtures on the crystallization of the amorphous $Fe_{75}Si_9B_{16}$ alloy, with the aid of electric and magnetic measurements. It is concluded that the solid solubility of the Ag in these alloys is very small, reaching 2 at% at most. Because of microsegregation, the presence of even these minimal admixtures accelerates the crystallization procedure.

1. Introduction

During the last decade much experimental research has been conducted, aiming at the optimization of the soft ferromagnetic properties of the amorphous Fe alloys, which are of importance for the industry; typical achievements are the so-called FINEMET nanocrystalline alloys (Fe-Cu-Nb-Si-B) [1] or the more recent NANOPERM ones (Fe-Cu-Nb-Zr-B) [2], where the improvement of the properties is mainly due to the ultrafine grain structure that the Cu admixtures cause, via microsegregation.

The influence of the Cu on the kinematics of the crystallization of the amorphous alloys Fe-Si-B has been studied in a previous paper [3]. In view of the fact that Ag has a stronger tendency than Cu to segregate [4], this paper studies the crystallization of the amorphous alloys having Ag admixtures through measurements of the saturation magnetization and of the electrical resistivity.

2. Experimental procedure

Amorphous ribbons of $Fe_{75-x}Ag_xSi_9B_{16}$, where $x = 1$, 2, 3 or 4, were prepared by melt-spinning; the ingots were prepared by arc-melting 3N+ pure materials in the appropriate ratios. The composition of the ribbons was verified by S.E.M./E.D.A.X as regards Fe, Ag and Si, whereas the atomic concentration of B was taken as equal to the value calculated during the preparation of the ingots.

The saturation magnetization (at $B = 0.5$ T) was measured with a vibrating sample magnetometer; the samples were ribbon fractions with a total mass of approximately 30 mg. The measurements were made either during the heating of the samples from room temperature up to 800°C at a rate of 3°C/min, or during a 24-hour heating at constant temperature. In the latter case the rate until the particular temperature was reached was 10°C/min.

The electrical resistivity from room temperature up to 900°C (at 3°C/min) was measured on 2-cm ribbons, using a four-contact dc method. Both the electric and magnetic measurements were repeated 2 or 3 times to minimize the errors introduced mainly by the inhomogeneity of the samples. All preparations and measurements were carried out in an Argon atmosphere.

3. Results and phenomenology

Fig. 1 shows the variation of the saturation magnetization of the alloys as a function of temperature; Fig. 2 shows the corresponding variation of the electrical resistance. In both figures the crystallization process is made evident by the increase of the magnetization and the decrease of the resistance.

Before discussing the crystallization effect we shall refer to some ferromagnetic characteristics of the amorphous and of the crystalline materials, in order to deduce some conclusions about the way both the initial state and the final product are affected by the Ag concentration.

Regarding the amorphous alloys, the Curie temperature is initially lowered with the concentration of the admixtures, then it increases. More specifically, this critical temperature is estimated to be 440, 432, 403, 412 and 426°C for the alloys with 0, 1, 2, 3 and 4 at% Ag correspondingly. The Curie temperatures was estimated from the turning points of the curves with an absolute error of ±2°C. Either the decrease or the increase in the Curie temperature, due correspondingly to the attenuation or accentuation of the interatomic exchange interactions, are common effects in Fe-based alloys having non-magnetic impurities. In the amorphous alloys Fe-Si-B, near this stoichiometry, the Curie temperature increases when the Fe concentration decreases [5]. Since in the alloys examined the Ag atoms substitute Fe ones, the gradual increase of the critical temperature could be explained. The observed complex behavior, though, in such a small concentration range suggests a rather inhomogeneous dispersion of admixtures throughout the amorphous material. Taking into account that the solid solubility of Ag in either Fe or B,

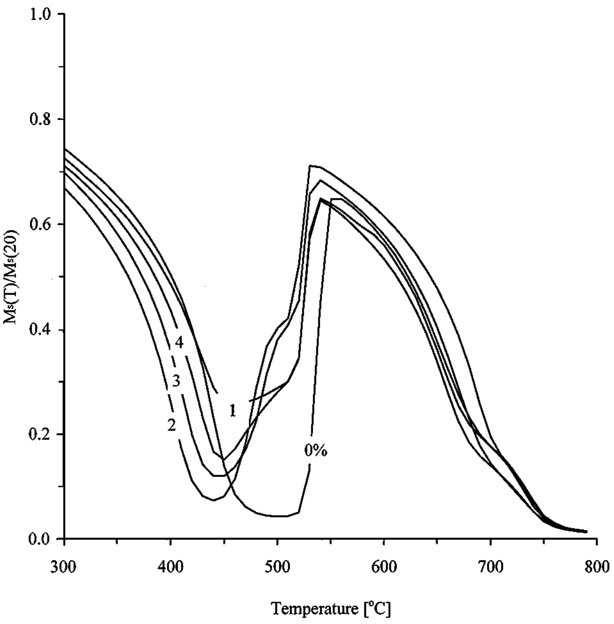

Figure 1 Variation of saturation magnetization as a function of temperature.

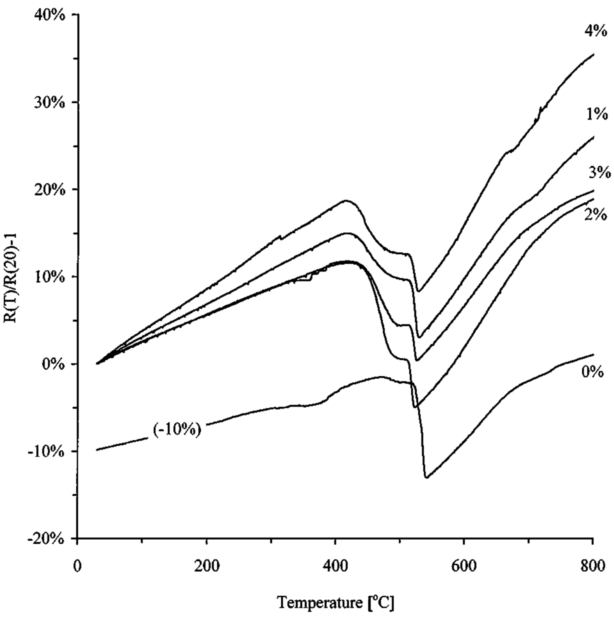

Figure 2 Variation of electrical resistance as a function of temperature.

or Si is insignificant even at very high temperatures [4], it is concluded that a random and homogeneous dispersion of the admixtures can be expected only at very low concentrations. On the contrary as the concentration increases, there will be regions rich in Ag and regions poor in it. Thus, the "effective" percentage of the admixtures (those that dictate the magnetic behaviour of the alloys) initially increases with the nominal concentration and then remains constant. If the Fe-Ag bonds favor the attenuation of the exchange interactions, one can explain the initial lowering of the Curie temperature and then the expected increase.

As regards the magnetic behaviour of the crystalline materials, two ferromagnetic phases are observed and, correspondingly, two Curie temperatures. The higher of these two is independent of the concentration of the admixture and is approximately 740°C, coinciding with that of the bct Fe_2B compound [6]. The final products of the crystallization of the amorphous Fe-Si-B alloys, at this particular stoichiometry, are bcc Fe[Si] and bct Fe_2B [6–8]. We are thus led to the conclusion that the first ferromagnetic phase is due to the formation of the bcc Fe[Si,Ag]. The Curie temperature of this phase initially increases with the concentration of the admixture and then decreases. More specifically, it is estimated from the curves of Fig. 1 to be 650, 658, 687, 668 and 654°C (±2°C) for the alloys with 0, 1, 2, 3 and 4 at% Ag correspondingly. The increase of the Curie temperature probably signifies the growth of purer bcc Fe regions, given that Si lowers the critical temperature, whereas the Ag impurities are expected to be concentrated along the grain boundaries, similar to Cu impurities [1].

Now, regarding the crystallization process, the measurements suggest that the presence of Ag admixtures induces an acceleration of the crystallization, displacing a stage of it towards lower temperatures; this stage manifests itself within a relatively wide temperature range (~100°C), whereas the crystallization is completed abruptly in a second stage, at higher temperatures. The greater the percentage of the material that becomes crystallized during the first stage, the lower the temperature at which the second stage occurs. The overall crystallization procedure is accelerated as the Ag concentration rises to 2 at% and then it is gradually decelerated. Suffice it to mention that the second crystallization stage takes place at 545, 528, 520, 524 and 528°C (±2°C) for the alloys with 0, 1, 2, 3 and 4 at% Ag correspondingly.

The same conclusions are arrived at by the measurements of the saturation magnetization during the heating of the alloys at constant temperatures. Measurements are carried at 400, 425, 450, 475 and 500°C. In Fig. 3 part of the experimental results is presented, regarding the isothermal variation of the magnetization at 475°C. As can be seen, for the alloys with no Ag admixture the crystallization procedure is completed in three stages. During these stages there take place

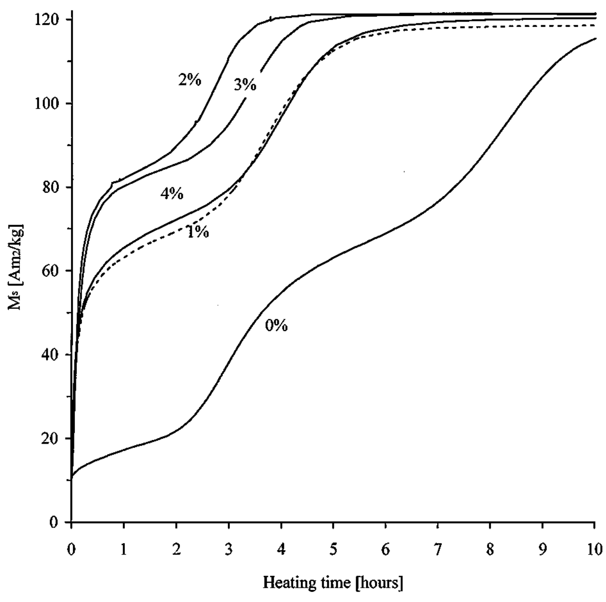

Figure 3 The isothermal variation of the magnetization of the alloys during their subjection to heating at 475°C.

correspondingly [7, 8] (a) the growth of dendritic bcc Fe[Si] and the nucleation of bct Fe_3B, (b) the eutectic crystallization of bcc Fe[Si] + bct Fe_3B and (c) the breaking of the metastable bct Fe_3B compound into bcc Fe and bct Fe_2B. From measurements carried out at 450°C with alloys having 1 at% Ag, three stages are also discerned, the first two of which take place almost simultaneously during the first minutes of heating. For all the other alloys, with greater Ag concentration, only two stages are discernible. The fact that the third stage for all the alloys starts when their magnetization reaches a definite value (80 Am^2/kg at 475°C, 60 Am^2/kg at 500°C), suggests that the presence of admixtures accelerates the second crystallization stage so that it takes place simultaneously with the first.

These measurements can lead to some calculations, under certain assumptions, in order to reach some conclusions regarding the initial crystallization rate [9]. Thus, by assuming that the first regions formed are bcc Fe[Si], the crystallization rate during the first minutes of heating can be determined (Fig. 4). Given a good agreement with the Arrhenius equation, the activation energy and the pre-exponential frequency factor versus the Ag concentration are plotted in Fig. 5, by fitting the results. It should be noted that the overall image remains qualitatively unaltered and there are no significant quantitative changes, when the Fe concentration in the initially formed crystalline regions is varied from 80 to 100%.

It is seen that both the activation energy and the pre-exponential frequency factor increase with the Ag concentration until the latter reaches 2%, then they decrease. The change in the activation energy is relatively small; the values given in the literature [8, 10] vary from 150 to 300 kJ/mole. On the contrary, the change of the frequency factor is several orders of magnitude. It thus becomes obvious that it is the latter that primary dictates the crystallization rate.

The frequency factor, as a physical quantity, expresses the maximum possible rate of formation and growth of the crystalline regions. The insignificant solid solubility of Ag favors microsegregation in the amorphous alloys and, by extension, causes this factor to increase; in view of what was said about the concentration of the "effective" admixtures, the variation of the factor with the nominal concentration of Ag can be accounted for.

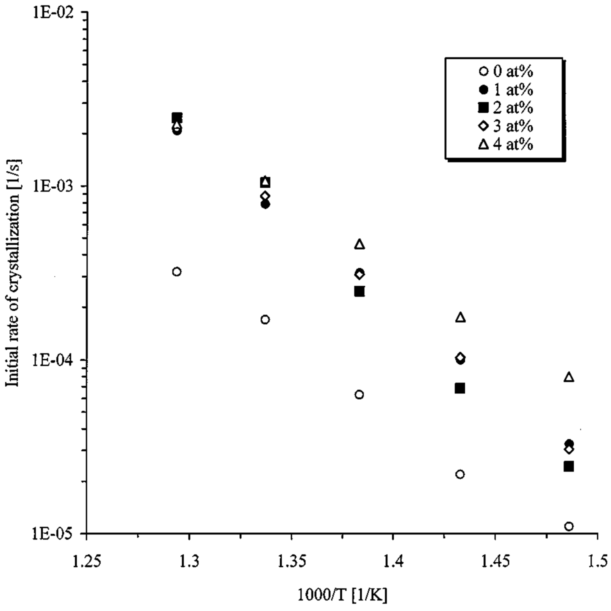

Figure 4 Initial crystallization rate of alloys vs. temperature.

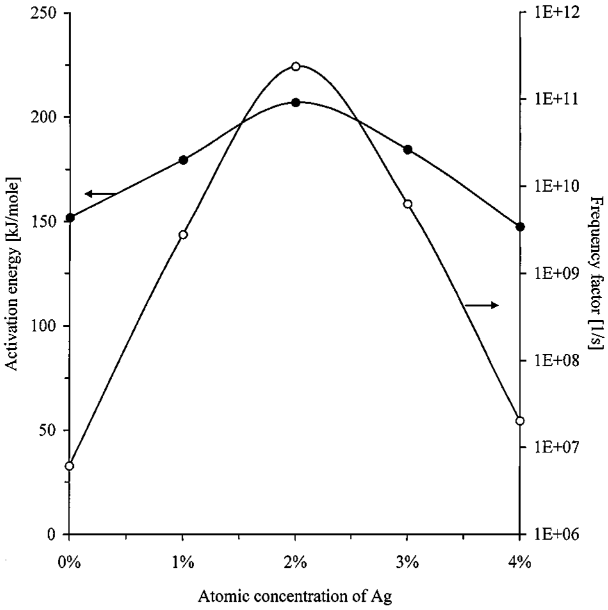

Figure 5 Activation energy and pre-exponential frequency factor for bcc Fe[Si] crystallization vs. the concentration of Ag admixtures.

The kinematics of the eutectic bcc Fe[Si] + bct Fe_3B (second stage) depends on the ratio of B atoms to Fe ones in the remaining amorphous material. As the ratio increases, this stage is accelerated. The growth of bcc Fe[Si] at the first crystallization stage is accompanied by long range atomic diffusion and, consequently, by the enrichment of the amorphous material in B. The acceleration of the first crystallization stage results in a more rapid enrichment. Also, the replacement of the Fe atoms by Ag ones causes the ratio B/Fe to increase. The combination of these two effects results in the acceleration of the second crystallization stage with the Ag concentration.

4. Conclusions

It is seen that 2 at% Ag is a critical concentration as regards the crystallization behavior of the alloys under examination and it most probably represents the maximum solid solubility of Ag in these alloys. This concentration also corresponds to the maximum formation and growth rate of bcc Fe[Si] nuclei, which is one of the most important factors regarding the preparation of nanocrystalline materials. Comparing Ag to Cu as a candidate for admixture in Fe-Si-B alloys, we see that Ag induces a slower nucleation than Cu [3]; this, coupled with the higher price of the Ag, makes silver less attractive for production.

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