Influence of Ag admixtures on the crystallization of amorphous Fe$_{75}$Si$_9$B$_{16}$

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This work studies the influence of the Ag admixtures on the crystallization of the amorphous Fe$_{75}$Si$_9$B$_{16}$ 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$Ag$_x$Si$_9$B$_{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 $3^\circ$C/min, or during a 24-hour heating at constant temperature. In the latter case the rate until the particular temperature was reached was $10^\circ$C/min.

The electrical resistivity from room temperature up to 900°C (at $3^\circ$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 $\pm 2^\circ$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,
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 Fe₃B 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 Fe₂B [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, 668, 664°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