

EFFECTS OF TUNGSTEN ADDITION ON CRYSTALLIZATION, MAGNETIC AND ELECTRICAL TRANSPORT PROPERTIES OF AMORPHOUS $\text{Fe}_{81-x}\text{W}_x\text{Si}_9\text{B}_{10}$ ALLOYS

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The work is focussed on the influence of tungsten on magnetization, electrical transport resistivity, crystallization process and conditions of its optimisation in amorphous Fe-W-Si-B alloy. The samples were melt-quenched ribbons 24 μm in thickness and 12-15 mm in wide. The structure was checked by XRD. The microstructure was evidenced for as-cast and annealed sample by TEM and ED. The magnetization and electrical resistivity were made *in-situ* during sample annealing between 300 K and 1100 K. The Curie temperature was estimated from the inflexion point of the first rapid demagnetization. For electrical resistivity measurements the conventional four-probe DC technique was used. The crystallization temperatures were determined from temperature dependence of magnetization and electrical resistivity. In the samples without or with low W content, lower than 5.5 at %, the precipitation of α -Fe in a first crystallization step started earlier than it was expected and it was accelerated probably by the formation of a solid solution phase saturated with bor. During second crystallization step Fe (W)-B small crystallites larger in size but less in the percentage than of α -Fe (W) phase are formed. The W addition at the expense of Fe causes the Curie temperature of Fe-W-Si-B alloys to decrease significantly.

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1. Introduction

The amorphous-to-crystalline transformation of metallic glasses has received large attention because of fundamental interest in understanding their structural and physical properties and because of potential application in relation to their thermodynamic properties. A lot of studies were carried out on structural relaxation and on the evolution of the magnetic properties as a function of the annealing time and of the annealing temperature [1-2].

For amorphous alloys of the Fe-TM-M type (TM-3d transition metal, M-one or more of the so-called metalloids) has been shown to increase thermal stability, decrease the Curie temperature, T_c , and seems well suited for measurements of magnetic properties and electrical resistivity [3-4]. Particularly, for Fe-Si-B amorphous system, the nature of the crystalline phase formation during annealing is strongly dependent upon the chemical composition and upon the thermal annealing conditions [5]. Moreover, the magnetic properties of ferromagnetic amorphous (Fe-TM)-Si-B alloys vary with the alloying of transition metals (TM) like V, Cr, Mo and others [6-7]. Generally, little has been known about the microstructure, magnetic and electrical resistivity in Fe-W (Si)-B amorphous alloys and the phases resulted as a consequence of thermal treatment. However, it is known that

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evolution of the soft magnetic properties in Fe-W-B alloys is closely related to alloy microstructure evolution during amorphous-crystalline phase transition process [8-10]. Also, it was confirmed that a necessary condition for good soft magnetic property maintenance is a high Curie temperature of the residual amorphous phase [10]. It was shown that alloying element addition in Fe-Si-B based alloys can change the mechanism of nucleation or growth rate of the nanocrystalline phase [11-13]. Consequently, magnetic properties of the material as well as the electrical properties are strongly influenced by conditions of thermal annealing (temperature/time) leading to the formation of a nanophase. The appropriate alloy chemistry and conditions of thermal annealing allow the production of material with desirable physical properties for particular applications.

The goal of this paper is to study the influence of W substitution for Fe on saturation magnetization, electrical resistivity, crystallization process and conditions of its optimisation in amorphous Fe-W-Si-B alloy.

2. Experimental

Experiments were carried out on samples of the following amorphous alloys: $\text{Fe}_{81}\text{Si}_9\text{B}_{10}$ (based alloy), $\text{Fe}_{78.5}\text{W}_{2.5}\text{Si}_9\text{B}_{10}$, $\text{Fe}_{75.5}\text{W}_{5.5}\text{Si}_9\text{B}_{10}$ and $\text{Fe}_{74.5}\text{W}_{6.5}\text{Si}_{2.5}\text{B}_{10}$. All samples were obtained by melt spinning technique in pure Ar-atmosphere in the form of ribbons with thickness of about 24 μm and wide of 12-15 mm. The structure of samples was checked by X-ray diffraction (XRD) with $\text{CuK}\alpha$ radiation ($\lambda = 0.15405 \text{ nm}$). The microstructure of as-cast and annealed samples was evidenced by transmission electron microscopy (TEM) and electron diffraction (ED). The mean grain size was estimated by using Scherrer's formula from the half-width of bcc-Fe (110) reflection peak. Slow scans were performed around the (110) reflection peak and each scan were corrected for $\text{K}\alpha$ spectral and instrument broadening by a computer implementation of Stokes procedure [14]. The crystallization temperatures were determined from temperature dependence of magnetization and electrical resistivity in their inflexion points corresponding to the rapid change in magnetization and, respectively, in electrical resistivity.

The saturation magnetisation of the as-cast and annealed samples has been measured with a computer assisted torque-magnetometer (TQM) [15] with 1T external magnetic field. The examinations of the crystallization process were carried out *in-situ* by means of saturation magnetization during the temperature increasing up to 1100 K using 4 K/min heating rate. The annealing temperature programming and control was made with an accuracy of $\pm 1\text{K}$ through an electronic system [16].

The Curie temperatures, T_c , were determined as the temperatures corresponding to the inflection point in the region of the first rapid magnetization decrease.

For electrical resistivity measurements the conventional four-probe DC technique was used in the temperature range from room temperature up to 1100 K.

3. Results

The all as-cast alloys were in amorphous state and this was confirmed by XRD, TEM and ED measurements. Fig. 1a shows the microstructure TEM image while Fig. 1b corresponds to the selected area electron diffraction (SAED) pattern obtained for the as-cast $\text{Fe}_{74.5}\text{W}_{6.5}\text{Si}_9\text{B}_{10}$ alloy.

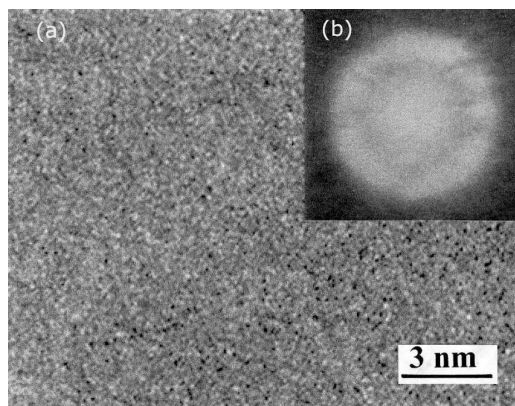


Fig. 1. (a) Transmission electron microscopy (TEM) image and (b) selected area electron diffraction (SAED) pattern obtained for the $\text{Fe}_{74.5}\text{W}_{6.5}\text{Si}_{2.5}\text{B}_{10}$ alloy in the as-cast state.

Fig. 2 shows the TEM images and the corresponding SAED patterns for samples annealed at different temperature as follows: (a) $\text{Fe}_{81}\text{Si}_9\text{B}_{10}$ alloy annealed at 850 K; (b) $\text{Fe}_{78.5}\text{W}_{2.5}\text{Si}_6.5\text{B}_{10}$ alloy annealed at 950 K, (c) $\text{Fe}_{81}\text{W}_{5.5}\text{Si}_{3.5}\text{B}_{10}$ alloy annealed at 1000 K and (d) $\text{Fe}_{81}\text{W}_{6.5}\text{Si}_{2.5}\text{B}_{10}$ alloy annealed at 1050 K. No Fe-W compound was identified by TEM.

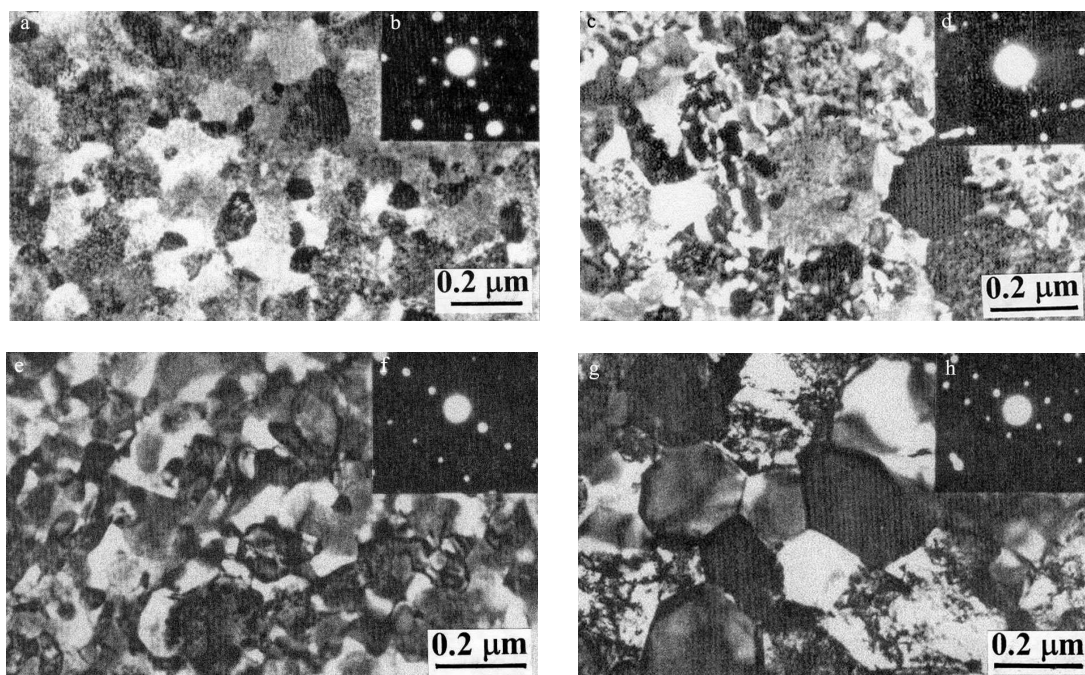


Fig. 2. Transmission electron microscopy (TEM) images and selected area electron diffraction (SAED) patterns: (a) $\text{Fe}_{81}\text{Si}_9\text{B}_{10}$ alloy annealed at 850 K; (b) $\text{Fe}_{78.5}\text{W}_{2.5}\text{Si}_6.5\text{B}_{10}$ alloy annealed at 950 K, (c) $\text{Fe}_{75.5}\text{W}_{5.5}\text{Si}_9\text{B}_{10}$ alloy annealed at 1000 K and (d) $\text{Fe}_{74.5}\text{W}_{6.5}\text{Si}_9\text{B}_{10}$ alloy annealed at 1050 K.

From TEM images in Fig. 2 and, additionally, from the corresponding XRD patterns it was determined the ferromagnetic grain size, which was between 50 nm and 200 nm as a function of W content: 0-6.5 at. %.

Fig. 3 shows the saturation magnetisation, M_s (T) as a function of temperature for all investigated samples. It is obvious that Curie temperature, T_c , decreases with the addition of tungsten. It is clearly seen from Fig. 3 that a two step crystallisation occurs for all the samples.

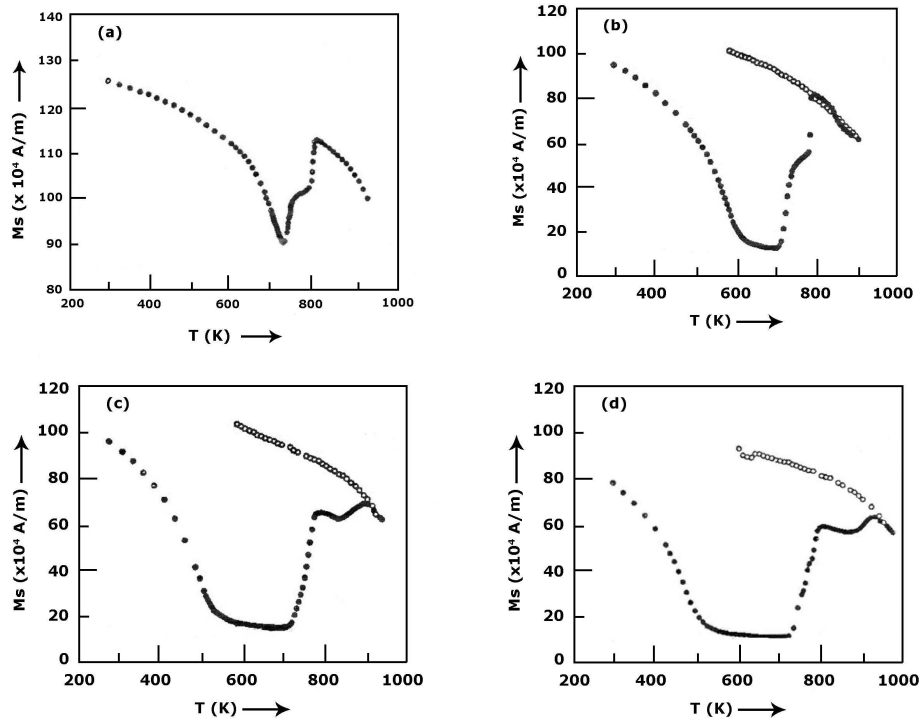


Fig. 3. Saturation magnetisation as a function of increasing temperature, using 4 K/min heating rate, in external field of 1T for (a) $\text{Fe}_{81}\text{Si}_9\text{B}_{10}$ (based alloy), (b) $\text{Fe}_{78.5}\text{W}_{2.5}\text{Si}_9\text{B}_{10}$, (c) $\text{Fe}_{75.5}\text{W}_{5.5}\text{Si}_9\text{B}_{10}$ and (d) $\text{Fe}_{74.5}\text{W}_{6.5}\text{Si}_9\text{B}_{10}$.

The electrical resistivity ρ of the samples was measured with increasing temperature up to 1100 K. A plot of ρ as a function of the temperature for all amorphous alloys is shown in Fig. 4.

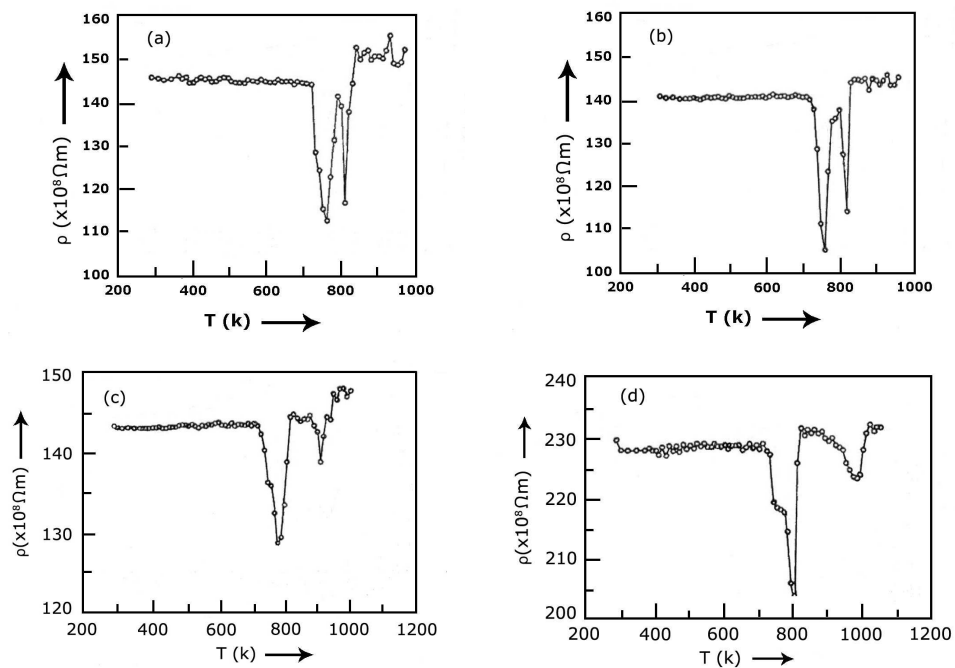


Fig. 4. Electrical resistivity ρ against temperature for (a) $\text{Fe}_{81}\text{Si}_9\text{B}_{10}$ (based alloy), (b) $\text{Fe}_{78.5}\text{W}_{2.5}\text{Si}_9\text{B}_{10}$, (c) $\text{Fe}_{75.5}\text{W}_{5.5}\text{Si}_9\text{B}_{10}$ and (d) $\text{Fe}_{74.5}\text{W}_{6.5}\text{Si}_9\text{B}_{10}$.

The two step crystallisation for all alloy compositions is evident from the curves of Fig. 4.

The drop in the resistivity at the first step is more pronounced than at the second and lies in the range between $141 \times 10^8 \Omega\text{m}$ and $105 \times 10^8 \Omega\text{m}$ for an alloy with 2.5 at. %W. For the second step resistivity drops from 231×10^8 to $224 \times 10^8 \Omega\text{m}$ were measured for an alloy with 6.5 at. %W. The first step crystallisation takes place through a broad temperature range (30 to 60 K) depending on the W concentration. The difference of temperature between the first and second step of crystallisation also depends on the W concentration. The knee in the ρ (T) curves corresponds to inflexion points in the sharp rise region of the M_s (T) curves.

The Curie temperatures and crystallisation temperatures, T_{x1} and T_{x2} , which were determined from magnetic and resistivity measurements are given in Table 1.

Table 1. Curie (T_c) and crystallisation temperatures for the first (T_{x1}) and second (T_{x2}) crystallisation peaks for Fe-W-Si-B alloys.

Sample	T_c (K)	T_{x1} (K)		T_{x2} (K)	
<i>Chemical composition</i>	<i>Magnetic</i>	<i>Magnetic</i>	<i>Resistively</i>	<i>Magnetic</i>	<i>Resistively</i>
Fe ₈₁ Si ₉ B ₁₀ (based alloy)	720	735	761	774	806
Fe _{78.5} W _{2.5} Si ₉ B ₁₀	630	725	750	770	810
Fe _{75.5} W _{5.5} Si ₉ B ₁₀	570	770	806	915	936
Fe _{74.5} W _{6.5} Si ₉ B ₁₀	522	762	795	905	924

4. Discussion

Addition of W causes an increase of number of nucleation centres during thermal crystallization process. The crystallization temperature of the new alloy, comparatively with those of based alloy- Fe₈₁Si₉B₁₀ increases and this increase is higher when the added tungsten content with relatively large atomic radius is higher. Generally, the addition of an element with relatively large atomic radius causes a slowing down of growth rate of nanocrystalline α -Fe (Si) [17]. Therefore, the W addition, which atomic radius is approximately 17 % larger than Si atomic radius, makes easier the formation of α -Fe nanocrystalline phase by thermal crystallization from an amorphous precursor. The microstructure investigation confirms this affirmation (see, Fig. 2). In the case of alloy without or with low W content, lower than 5.5 at. %, an α -Fe (W) precipitation and Fe (W)-B phase formation simultaneously was evidenced. For alloys with higher W content, Fe (W)-B phase tends to decompose in bcc-Fe phase that becomes dominant in the alloy and extraordinary large precipitates of bcc-Fe can be detected by TEM investigations (Fig. 2g). The decomposition of the Fe (W)-B residual amorphous phase leads to an abrupt grain coarsening of the bcc-Fe (α -Fe) phase (Figs. 2g and 2h). During the crystallization process, the alloys of composition lower than 5.5 at % W exhibited a different behaviour, as compared with those had higher 5.5 at % W (see, Fig. 3 and Fig. 4).

For Fe₈₁Si₉B₁₀ (based alloy) and Fe_{78.5}W_{2.5}Si₉B₁₃ alloys the crystallization started at about 35 K earlier than of samples with higher W content. For Fe_{75.5}W_{5.5}Si₉B₁₃ and Fe_{74.5}W_{6.5}Si₉B₁₃ alloys two clearly distinguishable steps of crystallization were visible. The first step (770 K and, respectively, 760 K) corresponds with α -Fe (W) precipitation and Fe (W)-B phases formation. At a temperature of about 850 K and for 1h annealing in both samples, the Fe (W)-B phase tends to transform in α -Fe. The different behaviour of the first step of crystallization in the two groups of alloys can be satisfactorily explained on the basis of the well known phenomenon of quenched-in nuclei during solidification of the amorphous materials [18]. The existence of a certain chemical short-range ordering even in the liquid state between iron and boron atoms, forming clusters facilitates the early stage crystallisation by a mechanism described elsewhere [19]. According to this mechanism, nanocrystalline domains of an iron-like structure containing a high level of boron atoms gradually increase in size. Among the domains, those which happen to grow to a critical size (~ 5 nm) may become nuclei of α -Fe precipitates supersaturated in boron. Further growth of this nuclei

proceeds by including neighbouring domains, of supersaturated solid solution of boron in α -Fe. It is most probable that strain energy due to the boron atoms included in the α -Fe nuclei favour the further growth. In the case of alloys with 5.5 and 6.5 at % W the solid solution of tungsten atoms in the iron nuclei does not permit the formation of the clusters mentioned above, hence nucleation growth by the described mechanism is hampered.

5. Conclusion

The main conclusions of the present paper can be summarised as follows. (1) Nanocrystallization behaviour depends on W concentration and two groups of alloys with different crystallization behaviour were observed. In the samples without or with low W content, lower than 5.5 at %, the precipitation of α -Fe in a first crystallization step started earlier than it was expected and it was accelerated probably by the formation of a solid solution phase saturated with bor. The crystallization process in the first crystallization step consists in α -Fe (W) precipitation and Fe (W)-B phases simultaneously formation. During second crystallization step Fe (W)-B small crystallites larger in size but less in the percentage than of α -Fe (W) phase are formed. (2) The W addition at the expense of Fe causes the Curie temperature of Fe-W-Si-B alloys to decrease significantly. The phenomenon is compared with those of Fe-based alloys in which W replace iron atoms. (3) The variation of the saturation magnetization is less considerable than that of the Curie temperature. (4) For higher W concentration (6.5 at. %) a significantly increase of electrical resistivity takes place.

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