MELT SPUN Fe-Co-Cr-B-Si ALLOYS ELECTRICAL, MAGNETIC AND THERMAL PROPERTIES CHARACTERIZATION

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Aliajele amorfe sunt materiale cu proprietăţi magnetice şi electrice deosebite. Aceste proprietăţi sunt legate de compoziţia chimică a aliajelor amorfe, tehnologia de fabricaţie aplicată, starea suprafeţelor benziilor obţinute, tratamentele termice aplicate, etc.

Scopul acestei lucrări este să prezinte rezultatele cercetărilor cu privire la influenţa compoziţiei chimice şi a tratamentelor termice asupra proprietăţilor magnetice şi electrice a câtorva din aliajele sistemului Fe-Co-Cr-B-Si. Materialele aflate atît în stare amorfă cît şi după tratamentele termice aplicate la diferite temperaturi, au fost investigate folosindu-se următoarele metode: difracţie cu raze X, spectroscopie Mössbauer, analiza termică diferenţială, tehnica Bitter şi microduritate.

The amorphous alloys are materials with superior magnetic and electrical properties. These properties are influenced by the chemical composition, the heat treatment state, the surface condition, the production technology, etc

The goal of this paper is to present the research results of the effect of the chemical composition as well as the impact of temperature (ranging from -160 to 740^{o}C) on the magnetic and electrical properties of some alloys from the Fe-Co-Cr-B-Si system. The material in amorphous state and in different heat treatment states was investigated. The X-ray diffraction, Mossbauer spectroscopy, differential scanning calorimetry, Bitter technique and microhardness methods were used.

Keywords: Amorphous alloy, electrical resistivity, magnetic properties, crystallization temperature

1. Introducere

Amorphous alloys are metallic materials with a disordered atomic-scale structure. In contrast to most metals, which are crystalline and therefore have a highly ordered arrangement of atoms, amorphous metallic have a disordered atomic-scale structure. For both practical and theoretical reasons, amorphous metal alloys are an important class of materials. Their special magnetic, electrical, corrosion properties have led to a large variety of industrial applications [1].

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Depending on temperature the electrical resistivity shows a series of anomalies, especially around temperatures where first or second range transitions take place [2]. At low temperatures the electrical resistivity should tend to zero, but due to the structure defects and impurities, it tends to a constant value, bypassing the linear dependence. If the impurities presented in a certain metal have an electronic spin, then the electrical resistivity shows a minimum or a maximum characteristic. This behaviour is known as Kondo effect.

Rein et al [3] have studied the electrical resistivity of some alloys of Metglas-type under temperatures variation between 1.5 and 800 K as well as the influence of the crystallization on the electrical resistivity.

The authors have noticed a minimum value of electrical resistivity in the case of the above mentioned alloys. It was also noticed that between the temperature of ρ_{min} and the Curie temperature there is not any correlation.

The electrical resistivity of the amorphous and crystalline phases in the vicinity of T_{cr} (critical temperature) is relatively low. That means the basic contribution to the modification of the electrical resistivity is introduced through the chemical disorder and not through the material structure.

In the case of Metglas alloys it was also noticed that the crystallization causes the further modification of the minimum electrical resistivity.

Komatsu et al [1] have studied the variation of the electrical resistivity as function of the chemical composition of $(Co_{1-x}Fe_x)$ $Si_{10}B_{15}$ metallic glasses. The modifications of the resistivity behaviour in the case of quenched and pre-annealed samples were discovered to depend very much on the Co/Fe ratio. The annealed cobalt based amorphous metallic alloys have showed reversible modifications of the electrical resistivity. These results suggest that short distance order is powerfully influenced by the Co/Fe ratio**.**

Wolny et al [4] have carried out investigations on the $Fe_{40}Ni_{40}B_{20}$ amorphous alloy [5, 6] within the temperature range of 300-1100 K using heating rates of $85^oK/h$ and 170 K/h respectively. The dependences $\rho=f(T)$ are qualitatively different. The same team also studied the variation of the electrical resistivity during the isothermal annealing.

In addition to their special properties such as low volume shrinkage, high mechanical strength and hardness, low surface roughness, high resistance to corrosions the amorphous metallic alloys exhibit some unique magnetic properties such as high saturation magnetization and high permeability, which make them a good candidate for magnetic core materials in transformers and electrical motors [7].

The crystallization kinetics represents the limit at which these unique properties begin to deteriorate in the case of an alloy that exhibits excellent magnetic properties in its amorphous phase. Therefore, thermal stability determines the magnetic stability of the amorphous state of the material [8].

The variation of the saturation magnetization with temperature seems to be similar to that of a crystalline material. However, in the case of amorphous alloys the Curie temperatures are lower than in the case of crystalline materials, which somewhat limits their utilizations [9, 10]. Another advantage of the amorphous metallic materials is represented by their capacity to become magnetized in very weak magnetic fields.

2. Experimental Procedure

The amorphous $Fe_{75-x}Co_xCr_1B_7Si_{17}$ alloy ribbons, where x=1; 4; 7 and 10% at, prepared by single-roll melt-spinning technique, were about 25 - 32 μm thick and 2.0 mm wide.

In order to prepare stable amorphous alloys under given conditions for perspective applications it is desirable to understand the mechanisms by which a metallic glass crystallizes.

The dependence between electrical resistivity, temperature and cobalt content, was measured using samples of amorphous $Fe_{75-x}Co_xCr_1B_7Si_{17}$ alloys. The measuring range value was roughly between -160 and 750°C. Therefore, four-probe electrical resistivity measurement was conducted in an argon-atmosphere tube furnace with temperature fluctuation less than 2ºC for the range from 0 to 750°C. To determine the resistivity values at low temperatures from -160 to 0°C, the samples were immersed in liquid nitrogen. During the measurement a platinum thermocouple with the measuring range spanning values from -250 to 850°C was used. A Wheatstone bridge was used to determine samples resistivity values which were recorded at 10°C interval.

The used furnace has had also an external coil of copper wire which becomes magnetized when electricity is running through it. The furnace was built in such a way to give us the opportunity to study the influence of magnetic field on amorphous alloys properties, more exactly whether there are differences between the readings performed with and without a magnetic field.

The amorphous $Fe_{75-x}Co_xCr_1B_7Si_{17}$ alloy ribbons, where x=1; 4; 7 and 10% at., exhibit magnetic properties, therefore another set of samples have been chosen for studying their magnetic properties.

The goal of this paper was also to obtain an amorphous alloy with an enhanced saturation magnetic induction (B_S). The thermal stability determines the magnetic stability of the amorphous phase of the material. Therefore, for a better thermal stability of studied metallic glasses in the same time with saturation induction (B_S) enhancement, an enhancement of crystallization temperature (T_x) was also done. A better thermal stability of studied metallic glasses could facilitate the annealing in a magnetic field and also an extension of their industrial applications.

This will result in a higher crystallization temperature which enables the application of a heat treatment in order to eliminate internal stresses while keeping or even improving the magnetic properties without crystallization.

The Bitter technique or magnetic etching was applied and the magnetic domains of annealed metallic glass samples were highlighted. A drop of freshly prepared colloidal suspension of magnetite particles in a solution of glycerin and soap was found to be sufficient for each sample. Then this drop was spread into a thin layer over the surface of the sample by a cover glass, which also helped to avoid rapid drying of the colloidal suspension.

When a magnetic field parallel to the fiber axis was applied, the particles collected and agglomerated in regions where large stray fields of the sample were presented, typically over domain walls.

The magnetic hysteresis loops were also recorded using a ferrotester. The shape of the obtained curves may allow the values of the magnetic Bs, Br, Hc indices to be determined.

3. Results and discussion

The amorphous nature of the samples was confirmed by X-ray diffraction studies using Cu- Kα radiation. X-rays diffraction analysis showed that the alloy is in an amorphous state [5, 11], figure 1.

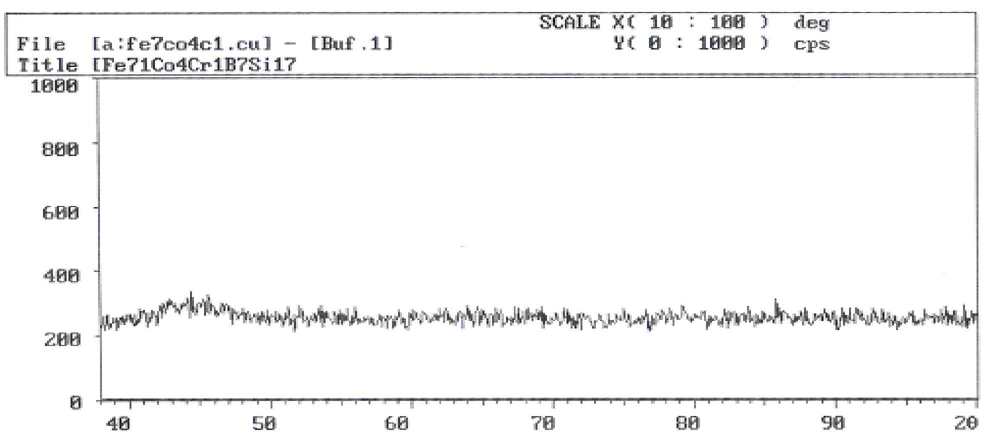


Fig. 1. $Fe_{71}Co_4Cr_1B_7Si_{17}$ alloy X-ray diffraction diagram

Figure 2 shows the variation of the electrical resistivity as function of temperature and cobalt percentage variation for the studied amorphous $Fe_{75-x}Co_xCr_1B_7Si_{17}$ alloys.

The electrical resistivity of the amorphous $Fe_{75-x}Co_xCr_1B_7Si_{17}$ alloys, (where x=1; 4; 7 and 10% at) is much higher than that of crystalline materials and it is in the same range as for the familiar nichrome alloys widely used as resistance elements in electric circuits.

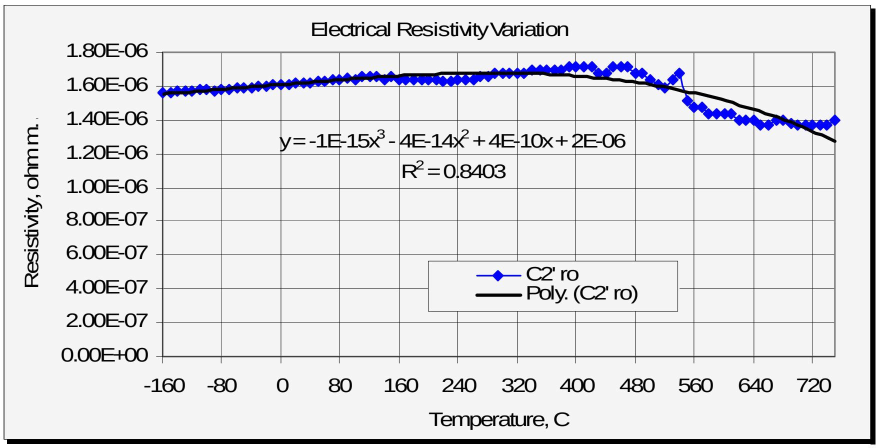


Fig. 2. Electrical resistivity variation of amorphous $Fe_{71}Co_4Cr_1B_7Si_{17}$ alloy versus temperature

Another interesting characteristic of the electrical resistivity of the alloys used in this experiment is that it does not vary much with temperature. The electrical resistivity of these alloys has slightly increased with increasing cobalt percentage.

However, a considerable drop of electrical resistivity is obvious at temperatures above 400°C. This drop is due to the process of crystallization. In fact, this resistivity drop emphasizes a critical point of each measured alloy. These critical points that could be also detected on the differential scanning calorimetry curves mutually coincide.

Due to their insensitivity to temperature variations for temperatures up to 400°C, these metallic glasses are suitable for applications in electronic circuits for which this property is an essential requirement [5, 12].

The curves of resistivity versus temperature exhibit a well defined knee about the Curie temperature of the crystalline state, T_x. The experimental results suggest that the anomaly of the electrical resistivity is due to the amorphous state.

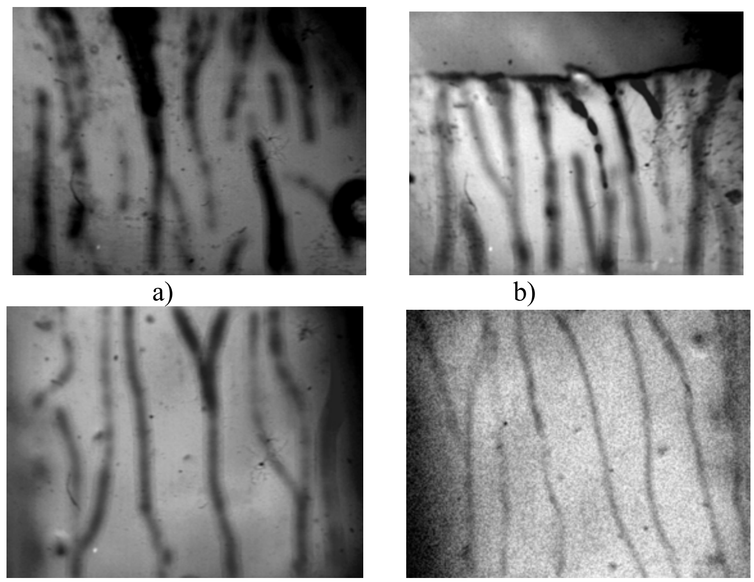
Large differences have been noticed in the Curie temperatures and the behaviour of the electrical resistivity between the amorphous and crystalline states [13].

In the design of power magnetic components a very essential element is the knowledge of the electrical and magnetic properties and characteristics of available soft magnetic core materials.

The sample's magnetization was controlled by the Bitter technique which can quickly provide information about the size and shape of the magnetic domains

[14, 15, 17]. The shapes of magnetic domains of the studied amorphous alloys are shown in figure 3.

Each domain is separated by magnetic domain walls where the magnetic moments gradually rotate from one domain to the next.



a) b)

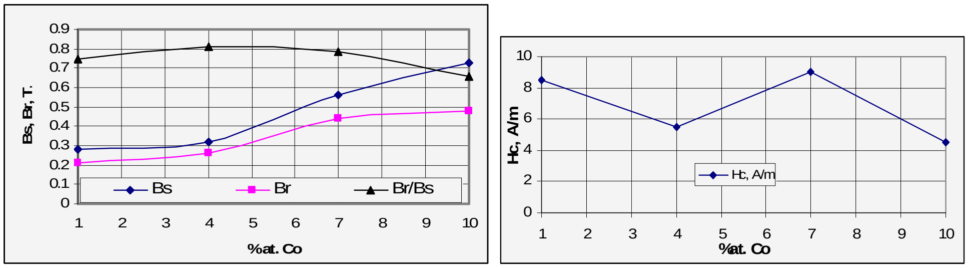
b) d)

Fig. 3. Magnetic domains highlighted through the Bitter technique for as-quenched state of the amorphous $Fe_{75-x}Co_xCr_1B_7Si_{17}$ alloys, x=1; 4; 7 and 10% at, (a to d)

The magnetic properties of amorphous alloys strongly depend on the domain structure and the behavior of the domain walls because they are at the “heart” of the process by which magnetic materials are magnetized and demagnetized [16, 17].

The magnetic domains are ribbon-type ones with a perpendicular orientation on the samples margin. The width of the domain wall is determined by the amorphous material nature. In figure 3 one can see that when the cobalt percentage increases the domain walls tend to become narrow. The domain walls become narrow also when the amorphization energy increases [14, 15].

The hysteresis loop, which describes the relationship between magnetizing force H and magnetic flux B generated in the magnetic amorphous alloys, shows that the saturation induction (Bs) and remnant induction (Br) increase when the cobalt percentage increases. A comparison of the *B-H* loops obtained for amorphous $Fe_{75-x}Co_xCr_1B_7Si_{17}$ alloys (x=1; 4; 7 and 10% at) with those of other amorphous alloys shows that they are comparable [18].



a) b)

Fig. 4. The variation of the magnetic properties

Besides the induction variation figure 4.a shows the influence of the cobalt content on the ratio of Br/Bs which reaches a maximum at 4% at Co. This ratio values stand above 0.5 which shows, that these materials are magnetically soft. The influence of the cobalt content on the coercive force (H_C) is also illustrated in figure 4.b. The coercive force (H_C) has the lower values for a content of 4 and 10% Co respectively.

The magnetic properties of amorphous alloys may be improved by annealing. Unidirectional anisotropy can be developed through heat treatment at temperature lower than the Curie temperatures, either under tension, or in a magnetic field. During the heat treatment a magnetic field was applied.

For identifying the primary and secondary crystallization temperatures, T_{x1} and T_{x2}, respectively, of the amorphous $Fe_{75-x}Co_xCr_1B_7Si_{17}$ alloys, differential scanning calorimetry (DSC) was used. Two heating rate of 5ºC/min and/or 10ºC/min during the annealing process have been applied.

Based on DSC (differential scanning calorimetry) curves of amorphous $Fe_{75-x}Co_xCr_1B_7Si_{17}$ alloys (x=1; 4; 7 and 10% at) alloys the critical temperatures have been obtained. On each DSC curve two exothermal peaks have been detected, the first one being the most intense [11].

Table 1 shows the value of the critical temperatures for all amorphous $Fe_{75-x}Co_xCr_1B_7Si_{17}$ alloys (x=1; 4; 7 and 10% at):

Table 1

Critical temperature

Alloy type	Heating rate, ºC/min	Heating temperature, ºC	Critical temperature, ºC	
			T_{x1}	T_{x2}
$Fe_{74}Co_1Cr_1B_7Si_{17}$	10	800	431	545
	5	1000	419	527
$Fe_{71}Co_4Cr_1B_7Si_{17}$	10	800	439	548
	5	1000	428	535
$Fe_{68}Co_7Cr_1B_7Si_{17}$	10	800	443	552
	5	1000	435	543
$Fe_{65}Co_{10}Cr_1B_7Si_{17}$	10	800	450	554
	5	1000	442	546

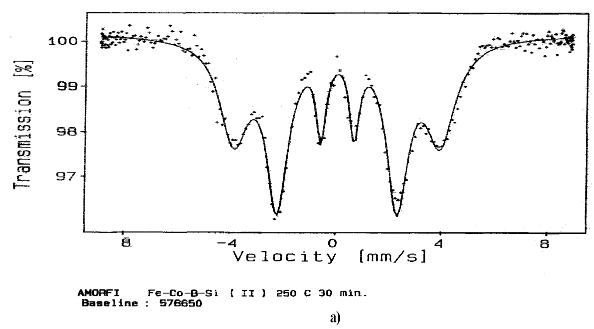
For faster annealing conditions (heating rate equal or superior to 10 K/min) only one peak was detected on the DSC curves, suggesting that the lower heating rate offers a more precise possibility to determine transformation temperatures [19].

It was shown that the peak temperature increases as the heating rate increases, suggesting a dependence of on the heating rate of the sample [20].

Tacking into account the derivative curve of electrical resistivity versus temperature one can conclude that it matches the DSC curve very well. The curve obtained by differential scanning calorimetry, for a heating rate of 5ºC/min for amorphous $Fe_{71}Co_4Cr_1B_7Si_{17}$ alloy, shows two peaks at about 435°C and 540°C which are the indication of some exothermal transformation [5].

Upon an optimal annealing crystallization the magnetization increases as well as the coercivity. The applied annealing can also produce their thermal stability [21, 22].

The crystallization kinetics of the magnetic amorphous alloys has a scientific interest for two important reasons. First of all, the crystallization kinetics represents the limit at which magnetic properties begin to deteriorate and second, a control over the crystallization kinetics allows to tailor the



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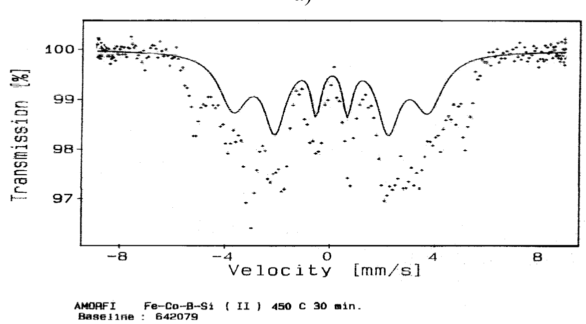


b)

Fig. 5. Mössbauer spectrum measured at 20°C of amorphous $Fe_{71}Co_4Cr_1B_7Si_{17}$ alloy after heating at 250°C (a) and 450°C (b) respectively for 30 minutes, heating rate of 5ºC/min

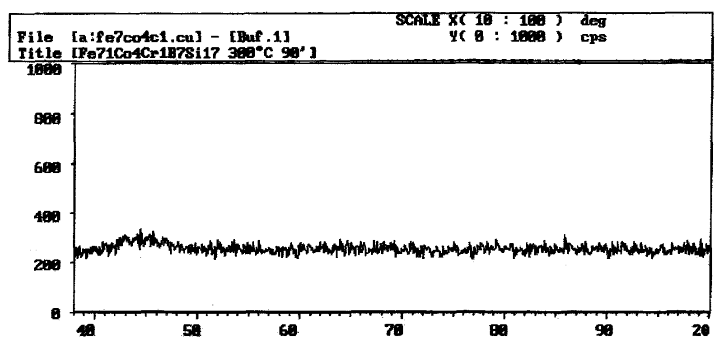
microstructure and to achieve the desired magnetic performance [9, 10].

The thermal stability of the amorphous alloys determines their magnetic stability. Annealing produces thermal stability against subsequent heat treatment, allowing annealed amorphous alloys to be used at low-temperatures even when they are cycled to temperatures as high as 500°C. A measure of thermal stability of an amorphous alloy is given by the crystallization temperature, T_x.

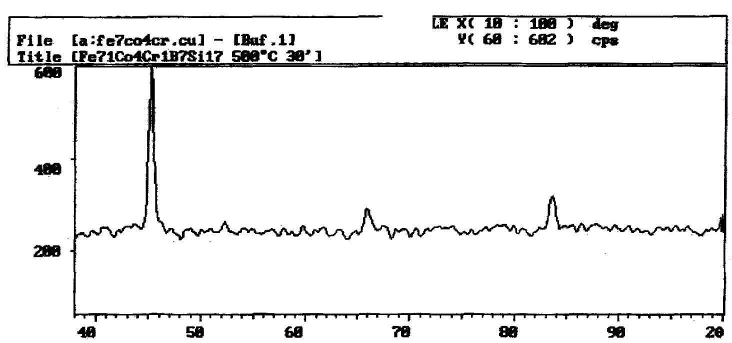
Heat treated samples of all amorphous $Fe_{75-x}Co_xCr_1B_7Si_{17}$ alloys (x=1; 4; 7 and 10% at) have been analyzed to point out the influence of heat treatments upon electrical, magnetic and structural properties of above mentioned alloys.

Subsequent heat treatment at 200; 250; 300; 350; 400; 450; 500°C; with exposure time of 30 minutes, in a neutral furnace atmosphere (Ar) in presence of a magnetic field were applied.

The Mössbauer spectrum for the amorphous $Fe_{71}Co_4Cr_1B_7Si_{17}$ alloy at room temperature, after heating at 250°C and 420°C for 30 minutes, is shown in Fig. 5. A well defined sextet shows that the local environment of the Fe is ordered



a)



b)

Fig. 6. X-ray diffraction diagrams of heat treated amorphous $Fe_{71}Co_4Cr_1B_7Si_{17}$ alloy
a) 90 minutes at 300º C; 30 minutes at 500º C

by the annealing process [24, 25].

The heat treated samples were again subject to diffraction analysis, figure 6. The diffraction analysis diagrams of the samples which were annealed below 450ºC are identical and reveal only a structure typical for the amorphous state. In the case of the sample annealed at 450°C the structure is still predominantly amorphous, but shows evidence of crystalline precursors [22]. It could be noted that the heat treatment of amorphous alloy Fe71Co4Cr1B7Si17 at 500°C for 30 minutes indeed result in some new chemical compounds [23].

The investigation carried out by Quivy et al [10] with respect to crystallization of the amorphous alloys Fe-B-Si-C indicates that this takes place in two stages.

According to [10] after annealing for 30 minutes at 450°C the first crystallization stage is completed. This stage corresponds to the appearance in the amorphous matrix of some Fe dendrites with low Si content, less than 1%. The second stage consists in the crystallization of the residual amorphous matrix enriched in B, Si, C which, subsequently becomes non-homogenous.

In the case of Fe-Co-Cr-B-Si samples, the phases of Fe(Si), Fe_2B and Fe_3B appear simultaneously between the Fe_{α} dendrites in the form of stratified crystals [22].

The composition of our alloys is not identical; however the transformation temperatures are very similar.

The microstructural and Roentgen analyses reveal crystals of some compounds only after annealing at 500°C for 30 minutes. Applying annealing at lower temperatures, even at longer times of exposure (60 or 90 minutes) does not modify the structure.

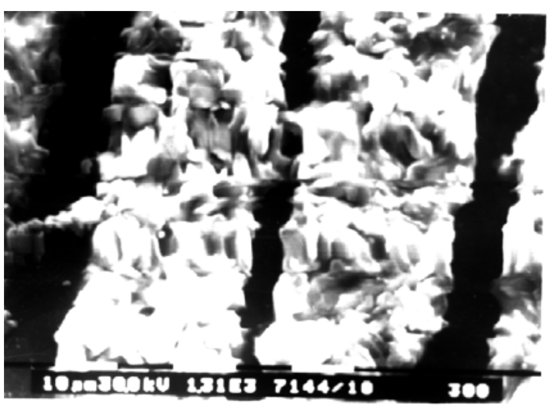


Fig. 7. SEM microstructure of a sample annealed at 500°C for 30 minutes, 500X

In agreement with the X-ray findings, thin sheet of annealed specimens at 500°C were found to contain FeB crystals in the amorphous matrix.

Fig. 7 presents SEM (scanning electron microscopy) microstructure of the amorphous $Fe_{71}Co_4Cr_1B_7Si_{17}$ alloy annealed at 500°C for 30 minutes. The number and size of FeB crystals increases with annealing time.

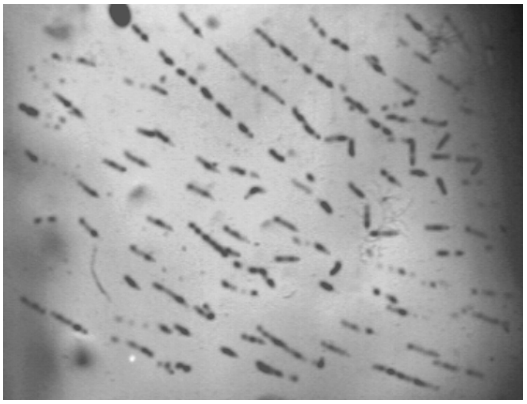


Fig. 8 Magnetic domains for the amorphous $Fe_{71}Co_4Cr_1B_7Si_{17}$ annealed at 400°C

The annealed samples at 400°C for 1/2 hour exhibit domains and were also analyzed using the Bitter technique (figure 8). Annealing induces a local magnetic anisotropy along the axis of the local magnetization. Where a domain wall exists during annealing, it will be stabilized in that position because moving it requires rotation of the local moments from their stable orientations [12, 26].

4. Conclusions

The amorphous nature of the samples was confirmed by X-ray diffraction studies using Cu- Kα radiation. X-rays diffraction analysis showed that the alloy is in an amorphous state.

The electrical resistivity of amorphous $Fe_{75-x}Co_xCr_1B_7Si_{17}$ alloys (x=1; 4; 7 and 10% at), has slightly increased with increasing cobalt percentage.

Heat treated samples of all above mentioned amorphous alloys have been analyzed to point out the influence of heat treatments upon their electrical, magnetic and structural properties.

A considerable drop of electrical resistivity is obvious at temperatures above 400^{o}C. This drop is due to the process of crystallization. In fact, this resistivity drop emphasizes a critical point of each measured alloy. These critical points that could be also detected on the differential scanning calorimetry curves mutually coincide.

The curves of resistivity versus temperature exhibit a well defined knee about the Curie temperature of the crystalline state, T_x

The magnetic domains are ribbon-type ones with a perpendicular orientation on the samples margin. The width of the domain wall is determined by the amorphous material nature.

The diffraction analysis diagrams of the samples which were annealed below 450ºC are identical and reveal only a structure typically to the amorphous state. In the case of the sample annealed at 450°C the structure is still predominantly amorphous, but shows evidence of crystalline precursors.

The microstructural and Roentgen analyses reveal crystals of some compounds after annealing at 500°C for 30 minutes. Applying annealing at lower temperatures, even at longer times of exposure (60 or 90 minutes) does not modify the structure. The number and size of FeB crystals increases with annealing time.

The studied amorphous metallic alloys are soft magnetic materials with a maximum saturation induction of ~0.8T, while the Br/Bs ratio values are above 0.5.

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