

Peculiarities of Surface Crystallization of Amorphous Ribbon from the Contact Side

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Abstract: Amorphous alloys are widely used in various fields of industry and technology to optimize their acquisition, as well as modern methods of their surface structure of the research complex, amorphous alloys, structure and mechanism of rotate kinematics study is required. The successful resolution of the issues of changing the physical and chemical properties of alloys, as well as their stability and thermal stability through changes in the content of specific recommendations to improve to prepare.

Keywords: crystallization, heat treatment, amorphous, magnet, thermal stability

1. Introduction

Surface crystallization amorphous ribbon with the contact side of the ribbon is a feature of some iron-based alloys. Conditions for obtaining the ribbon determine the maximum of the cooling rate of the surface on which the surface crystallization occur. This fact casts doubt on the hypothesis of the presence in the surface layers of the ribbon microcrystalline inclusions such as hardening of embryos. To determine the factors that determine their surface crystallization of the contact side of the ribbon, a study was conducted as the chemical composition of the surface layers of the ribbon, and studies of the kinetics of the surface crystallization. Investigating fusion liquid casting on a disc has been received by the method of strength. Funeral chemical composition is correspond $\text{Fe}_{58}\text{Ni}_{20}\text{Si}_9\text{B}_{13}$. Data of the bulk crystallization were taken from [1]. The annealing regime is selected so that the surface processes and the subsequent volume crystallization, obtained sufficiently developed for their identification by X-ray analysis. Figure 1 shows the X-ray diffraction and outer contact surfaces of the ribbon under investigation. Annealing regime have been illustrated, when the surface crystallization of fully hosted (1, a, b, c), the bulk crystallization, its development only in the isothermal holding, the corresponding mode of 1 g. X-ray analysis showed that in the case of the surface, and in the case of the first stage of the bulk crystallization occur an allocation of the solid solution based on $\alpha\text{-Fe}$.

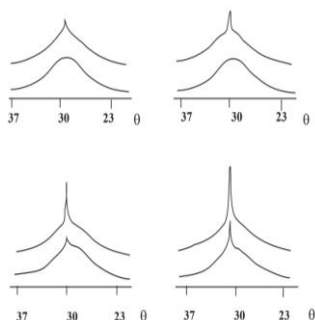
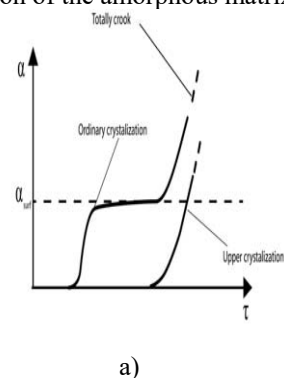


Figure 1: Diagram of diffractogramme changes of $\text{Fe}_{58}\text{Ni}_{20}\text{Si}_9\text{B}_{13}$ alloy at the surface (upper curve) and volume (lower curve) crystallization during isothermal annealing.

Changing of the degree of conversion of the amorphous phase (a) at the surface crystallization and crystallization kinetics of surface crystallization characteristics were investigated by X-ray analysis. Surface crystallization kinetics under isothermal conditions was analyzed using equation Mel Johnson-Avrami, based on formal kinetics theory. Index of the Avrami exponent was calculated as the value numerically equal to the slope of the line that describes the degree of conversion, in the coordinates $\ln(-\ln(1-x)) - \ln t$. Fig. 2 and represented 8-curves describing the kinetics of the surface and the initial stages of bulk crystallization. It can be seen that at the beginning surface crystallization occurs. After the complete transmission of the crystallization step occurs a period of stability formed amorphous-crystalline structure on the surface. At the end of this period have been developing processes of the bulk crystallization.

Analysis of the 8-shaped curves shows that, apparently no surface crystallization process is associated with the redistribution of the alloying elements diffusion in the bulk material. This is indicated by the fact the stability of the mixed amorphous-crystalline structure for some time. In the case of the redistribution of the element concentrations (diffusion enrichment of the surface layers of iron atoms during annealing) in the volume might occur processes that lead to the destabilization of the amorphous matrix.



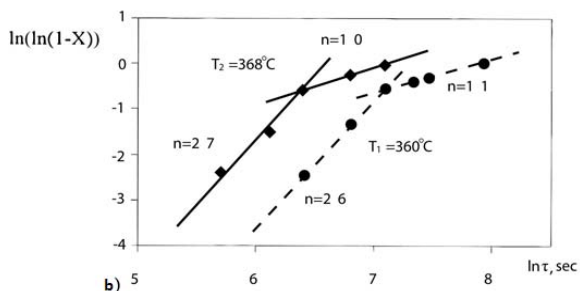


Figure 2: Kinetics of the surface crystallization in the coordinates of (a) - time (s) and coordinates of Mel-Johnson-Avrami (b) for the alloy $\text{Fe}_{58}\text{Ni}_{20}\text{Si}_9\text{B}_{13}$

Figure 2.6 shows the data for conversion by surface crystallization coordinates Mel-Johnson-Avrami at two temperatures. It is seen that the character of the lines in dependence on the temperature is not changed. In the both dependences observed inflection, and before and after the inflection point in the chosen coordinates the dependencies remain linear. This behavior is typical in the case of hopping transformation kinetics in time. Avrami index for the initial stages of the conversion is identical within the calculation error (± 0.1) and is equal to $n = 2.7$ and 2.6 , for isothermal annealing temperature equal to 360°C and 368°C , respectively. According to the theory of formal kinetics an indicator for the conversion, controlled by diffusion through the interface corresponds to the transformation, the development of which is determined by the simultaneous nucleation and growth of crystalline phase. When the conversion reaches 40%, the slope of the lines is changed, and the Avrami index value is changed to $n = 1.0$ and 1.1 at $T = 360^\circ\text{C}$ and 368°C , respectively. This value corresponds to the conversion, which is determined by the kinetics of the growth of existing nuclei. Such a change in the kinetics of the transformation can be explained by depletion of the near-surface zone of iron atoms, resulting in the formation of new nuclei of the crystalline phase is difficult, however, diffusion processes are sufficiently developed for the growth of existing crystals. Figure 3 illustrates the change in the chemical composition of the surface layers of the ribbon obtained by Auger electron spectroscopy.

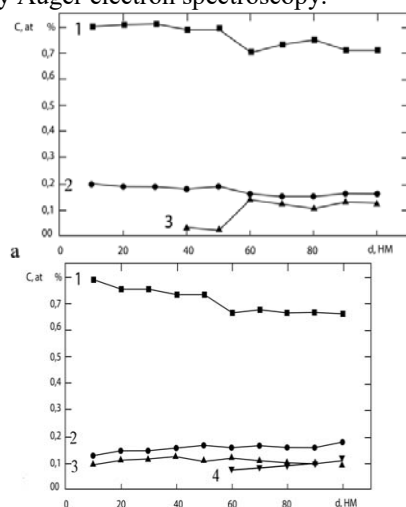


Figure 3: Change of the component concentration (C) of the depth (d nm) for $\text{Fe}_{58}\text{Ni}_{20}\text{Si}_9\text{B}_{13}$ alloy.

1 (■) - Fe, 2 (●) - Ni, 3 (▲) - B, 4 (▼) - Si

a - the contact surface of the belt. b-free surface.

It is seen that the chemical composition is different at different sides of the ribbon. However, common to both the surfaces is that concentration of iron and nickel is high as compared to the nominal. In both cases, the ribbon surface of the iron concentration reaches about 80 at.%. As the recess in the iron content of the material decreases, reaching 58% at about 100 nm. Nickel content varies little over the section of the surface layers of the ribbon. On the contact side concentration of the nickel corresponds to a nominal and is 20%, on the outside it is slightly lower (about 15%) and slightly changed over the cross section of the ribbon. Another situation is observed for the distribution of the cross section of the ribbon of the metalloid atoms. It can be seen that the outer layers of the ribbon at least solidified, the content of boron atoms in the cross section is close to the nominal, while the silicon is found in concentrations close to 9%, to a depth of only 60 nm. On the contact side of the ribbon metalloid content is less. Traces of boron appear only at a depth of 40 nm, then remained virtually unchanged. Silicon is not found up to a depth of 100 nm. Thus it is seen that the surface on which the observed surface crystallization depleted metalloid atoms. This phenomenon may be due to the type of microphase separation processes, developing during solidification of the casting ribbon during its on disk. It is known that doping alloy with atoms of metalloid increases thermal stability of the amorphous matrix. In this regard, depletion of surface layers metalloid atoms should lead to destabilization of the amorphous matrix near the contact surface of the belt. Changing the stability of the amorphous matrix and the high content of iron atoms in the surface layers of processes facilitate the formation of the crystalline phase, resulting in the preferential crystallization of the contact surface of the belt at low temperatures [2,3]. Shallow depth destabilized layer limits the development of the crystallization deep into the ribbon. Fig. 4 shows the dependence of surface crystallization of the investigated alloy in coordinates of $\ln \tau$, s - $1/T$, K⁻¹. Analysis of activation energy calculated from the slope of the line shows that the activation energy of surface crystallization is smaller than the activation energy of the volume crystallization. As for the volume crystallization of the alloy the total value of the activation energy is 300 kJ / mol [1]. Surface crystallization activation energy is 205 kJ / mol. Proceedings of linear dependencies respective surface and bulk crystallization, shows that lowering the temperature in the selected temperature range, the time gap between the onset of surface crystallization and volume increases. This suggests that despite of the reduction of the diffusion mobility of atoms and the associated increase in the time to the onset of crystallization, the formation of nuclei in the surface layers of the ribbon is facilitated. The main factor influencing nucleation in the surface layers is apparently distinct chemical composition of surface layer ribbon, the content in the bulk alloy ribbon corresponding nominal. Thus it is seen that crystallization processes in the surface layers of the investigated alloy material due to preparation technique. Features of technology of impact on the course of solidification of the ribbon, causing the segregation of alloying elements in the cross section. Changing the concentration of metalloid atoms influences the stability of

the amorphous matrix in the surface layers, which in turn leads to the relief nucleation process across the study area temperatures. To that fact indicates, the kinetics of formation of the crystallized layer, also. It is shown that the process of crystallization of the surface with the contact side of the belt is controlled by nucleation and growth processes. This transformation kinetics is not characteristic of a material having a ready centers of crystallization such as hardening of embryos.

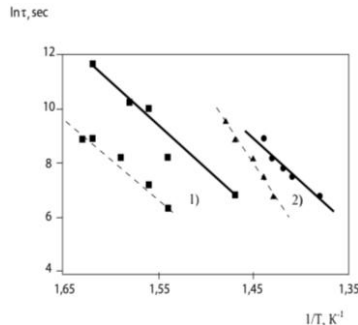


Figure 4: Logarithm of time before the surface (---) and bulk (-) crystallization ($\ln\tau$, s) against the reciprocal temperature ($1/T$ K $^{-1}$) for $\text{Fe}_{58}\text{Ni}_{20}\text{Si}_9\text{B}_{13}$ alloys (1) and $\text{Fe}_{77}\text{Ni}_1\text{Si}_9\text{B}_{13}$ (2).

Crystallization from the outer side of the ribbon: Not getting in contact with the disc side of the ribbon to be in the degraded conditions of the heat sink, which promotes the formation of a crystalline phase nucleation. Obviously, the amount of the crystalline phase will depend on the number of embryos quench, whose number depends on the rate of cooling the outer side of the belt, i.e. the technological features of the process for preparing amorphous material. To study the characteristics of surface crystallization processes in non-contact side of the ribbon were studied thermal stability during isothermal annealing. Also, the kinetics of surface crystallization have been investigated. Figure 5 shows the change in the type of test alloy X-rays on the outside, and hand contact during isothermal annealing. It is evident that both surface and volume crystallization of the investigated alloy goes with αFe release.

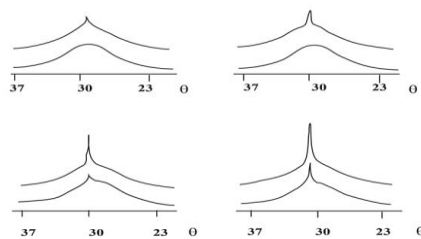


Figure 5: Scheme of changing the shape of the alloy $\text{Fe}_{77}\text{Ni}_1\text{Si}_9\text{B}_{13}$ diffraction patterns at the surface (upper curve) and volume (lower curve).

Analysis of the data showed that the surface layers of a non-contact side of the belt, there is a well-developed pore structure, consisting of several clearly visible fractions. The largest fraction is composed of pores with a size of about 100 nm. The presence of such structures also strives to have a strong influence on the crystallization processes, reducing the significance of the difference in specific volumes of factor amorphous and crystalline phases. The kinetics of surface

crystallization and a crystal phase dependent quantity of amorphous material on the annealing regime presented in Figure 6 in the Mel-Johnson-Avrami coordinates. From the 8-shaped curves in Figure 6a, seen that, as opposed to the contact surface on the side of the crystallization ribbon, in this case the volume of the alloy crystallization begins when the surface crystallization process is quite intense. Perhaps we can talk about the initiation of the crystallization process of bulk diffusion redistribution of alloying elements in the surface crystallization. This may be due to the processes of destabilization of the amorphous matrix modified chemical composition, or as a result facilitated the nucleation on the existing crystalline phase. Figure 6b shows the dependence of the degree of $\ln(-\ln(1-X))$, the conversion of the time ($\ln\tau$). Avrami index, determined from the slope of the line for a given temperature is $n = 0.9$ and 1.0 . This value is typical of Avrami index transformation, controlled growth of existing centers of crystallization. These data are in good agreement with the hypothesis of the presence of hardening of embryos in the surface layer on the outer side of the ribbon. The dependence of the time until the onset of crystallization reverse filamentary that surface crystallization on the outer side of the ribbon starts before the volume, and it is important to note that with decreasing temperature isothermal Extracts difference between the start of the processes of surface and volumetric crystallization decreases, to the point that when a certain temperature crystallization at surface and in the bulk material begin simultaneously. Calculation of the activation energy general crystallization process shows that the activation energy of surface crystallization (435 kJ / mol) exceeds the volume of the crystallization process (370 kJ / mol). Such a high crystallization activation energy is not conventional processes. Since the activation energy calculated by the appearance of the first reflections on the radiograph, contains as a component of the formation of the embryo, and the component of its growth, it is logical to assume that such a high value of the activation energy of the process provides one of the terms of the activation energy. This is shown in Figure 4.

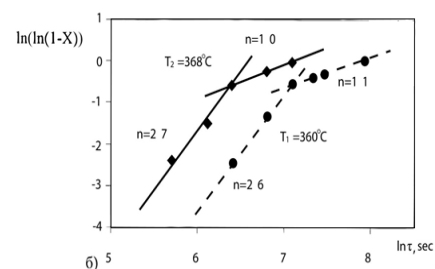
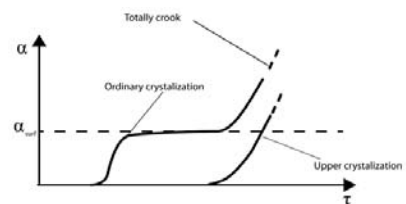
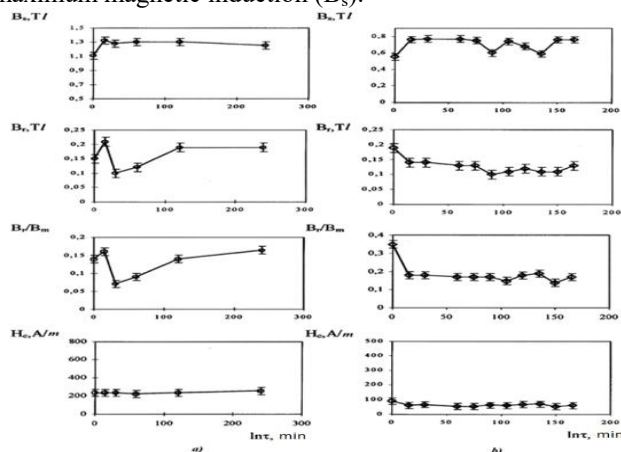


Figure 6: The kinetics of surface crystallization in degree of conversion coordinates (α) - time (s) and coordinates of Mel-Johnson-Avrami (b) for the alloy $\text{Fe}_{77}\text{Ni}_1\text{Si}_9\text{B}_{13}$.

In this case, apparently, the main contribution to the energy of activation contributes component associated with the growth of crystallites. This fact is indirectly confirmed by the fact that at a certain temperature the start surface and volume crystallization of the same. Reducing the diffusion mobility of atoms with decreasing temperature slows down the growth of the crystalline phase of the available embryos. At some critical temperature processes of nucleation and growth of crystalline phase (due to diffusion), in the amount of the material become as intense as the growth of crystals on the surface. Thus, it is seen that the preferential crystallization from non-contact side of the belt due to the presence of the crystal phase nuclei in the surface layers of the ribbon, formed by its obtaining.

Effect of surface crystallization on the magnetic properties of the material: Crystallization of the amorphous surface layers of ribbon material changes the structure and affect its physical properties. This is not only a violation of the uniformity of the material, but also with the emergence of additional stress fields in the cross section of the ribbon [4]. The test materials are characterized by a sufficiently large positive magnetostriction value, so for them the effect of surface crystallization on the magnetic properties is particularly noticeable.

Figure 7 a, b shows the dependence of the changes of the hysteresis loop parameters during isothermal annealing. It is evident that for the alloys change the maximum magnetic flux density is almost the same character. At low speeds in the amorphous matrix are developing processes of stress relaxation. Conducted in obtaining ribbon internal stresses due to changes in topological order, and annihilation of defects in the structure and the p-n-type are reduced significantly. As a result, there is some increase in the maximum magnetic induction (B_s).



This behavior is typical for both types of alloys. The behavior of the residual magnetic flux density and the square ratio of the alloys, however, the differences observed. If alloy Fe₅₈Ni₂₀Si₉B₁₃ B_m and B_m / B_r vary as well as B_s , and increased, then there is a decline Fe₇₇Ni₁Si₉B₁₃ alloy of these characteristics. Further annealing process leads to the development of surface crystallization. It is evident that due to magneto elastic effects B_s and B_r values plummet. This occurs as a result of the guidance material in uniaxial magnetic anisotropy directed perpendicular to the plane of

the ribbon. According to the theory It turns Morrish, this anisotropy is due to the induced voltage fields caused by the difference in specific volumes of amorphous and crystalline phases. This anisotropy changes the preferred direction of magnetization vectors of domains, resulting in a decrease in B_s and B_r . Accordingly, the observed drop in B_m / B_r . Thus, despite the guidance of additional stresses in surface crystallization occurs a change of the coercive force (H_c). Such a change in the hysteresis loop characteristic parameters for both alloys. Increasing the holding time at the annealing results in the relaxation induced voltages, whereby the value of the hysteresis loop parameters are returned to their original values. At the same time it is clear that there is a secondary alloy Fe₇₇Ni₁Si₉B₁₃ failure B_s and B_r . This is probably due to the complete annihilation of the available source material pore structure, whereby the voltage induced by subsequent surface crystallization stage relaxes considerably slower. Increasing the exposure time does not lead to changes in the parameters of the hysteresis loop until the beginning of bulk crystallization, when the fall occurs B_s and B_r and H_c increase as a result of developing the crystallization process.

Thus, it is clear that the phenomenon is caused by surface crystallization and is dependent on technological factors produce the material. Despite the fact that the investigated alloys are obtained by the same technology, a method of casting a melt in vacuum to a disk, they have observed differences in processes of surface crystallization.

2. Results

- 1) For materials of the first type is characterized by crystallization from the contact surface to the ribbon drive. This solidifies the first surface with a maximum cooling rate. The study of the chemical composition of the surface layers of the ribbon, as well as analysis of crystallization processes in the surface layers, showed that the surface layers of the ribbon are largely depleted metalloid atoms. As known, the doping atoms metalloids reduction leads to destabilization of the amorphous matrix. It is assumed that the phenomenon of micro-phase metalloids ribbon over the cross section is the main cause crystallization contact side
- 2) Analysis of the kinetics of crystallization showed that crystallization processes are controlled by nucleation and growth of new buds. It is interesting to note that the bulk crystallization process does not start immediately after the full completion of the conversion on the surface, but after some time. This indirectly indicates the fact that the bulk diffusion crystallization is not caused redistribution elements at the surface crystallization, as determined by the initial doping of the complex.
- 3) For the second type of alloys is characterized crystallization on the outer surface of the belt. The study showed the presence of near-surface layers of the developed pore structure. The presence of defects such as micro-pores (the largest fraction has a size up to 100 nm) can also affect the crystallization processes, reducing stress intensity guidance due to difference volume amorphous and crystalline phases.

- 4) Kinetics of crystallization showed that the surface crystallization of the corresponding conversion, controlled growth in existing appreciable amount of embryos. It is shown that the volume crystallization begins when the surface still has to develop. This fact shows the effect of diffusion processes, causing the surface crystallization on the stability of the amorphous matrix. Investigation of surface crystallization of alloys, as well as the activation of these processes energy analysis showed that crystallization from the outer surface has greater activation energy (435 kJ / mol) than the contact (205 kJ / mol). Moreover, this process has a higher activation energy than bulk crystallization process of the alloys (370 and 300 kJ / mol).
- 5) Based on the data, and based on the theory that describes the activation energy of the processes of nucleation and crystal growth processes, it is possible to conclude that the value of the activation energy of surface crystallization on the outer surface is mainly determined by the growth rate of reduction of existing hardening of embryos caused by low diffusion mobility of iron atoms. On this also indicates the fact that at a certain temperature is lowered, the time before the start of surface and bulk crystallization compares and processes of nucleation and growth, defining the bulk crystallization, are no less energetically favorable than the growth of existing nuclei.
- 6) In the case of the contact side of the belt of crystallization, phase separation in the preparation of the material provides a significant simplification of the process of nucleation, resulting in the activation energy for the surface crystallization of this type are mostly controlled by a term describing the process of nucleation of the crystalline phase.
- 7) The process of surface crystallization of the material structure change and accordingly changes its physical properties. This is especially noticeable in materials with a sufficiently high saturation magnetostriction, which include the investigated materials. During the crystallization of these materials due to magneto elastic effects can be induced magnetic anisotropy, resulting in a change in the parameters of the hysteresis loop. Hysteresis loops were conducted studies for changing the annealing, resulting in crystallization of the material surface.
- 8) The study found that, in accordance with the Eyring-Morrish in surface crystallization theory, due to the difference in specific volumes of the amorphous and crystalline phases in the material induced uniaxial magnetic anisotropy directed perpendicular to the plane of the ribbon. The impact of this type of anisotropy is seen to reduce the value of B_s , B_r and B_m/B_r in surface crystallization development.
- 9) The relaxation induced by stress leads to the return of the magnetic characteristics to the original values. Thus it is seen that the alloy, crystallizing the outside surface crystallization effect is less pronounced than that observed decline second magnetic characteristics. It is suggested that this is due to the influence of micro-porous structure in the surface layers of the ribbon.
- 10) A temporary increase in the hysteresis loop parameters caused not so much the development of relaxation

processes, as the presence of micro-pores, annihilating with the growth of the crystalline phase. The second is due to the decline of properties complete annihilation of the pores in the surface layer of the ribbon, thus again affecting surface tension induced crystallization.

- 11) The subsequent refund of the hysteresis loop parameters due to the development of relaxation processes. Furthermore, it is interesting to note that the surface crystallization, in spite of the additional guidance stress fields, changes in coercive force was observed.

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