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# Journal of Non-Crystalline Solids





# Formation of bcc nanocrystals in Co-based amorphous alloys



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### ARTICLE INFO

Key words: Amorphous structure Nanocrystals Crystallization Diffraction Electron microscopy

## ABSTRACT

The crystallization of amorphous alloys of Co-Fe-B-(Ti, Nb) system was studied by differential scanning calorimetry, X-ray diffraction, and transmission electron microscopy. It was determined that the alloying of amorphous alloys of Co-Fe-B system with elements having a bcc lattice promotes the formation of a metastable phase with this lattice during crystallization. Nanocrystal size and the fraction of the phase with a bcc lattice depend on the concentration of alloying components. When the concentration of bcc components increases, nanocrystal size decreases. When Nb (an element with a bcc lattice) is replaced by Ti (an element with an hcp lattice), the fraction of the bcc phase decreases, and multiphase crystallization (simultaneous formation of several crystalline phases) occurs. In  $Co_{56}Fe_{16}B_{20}Ti_8$  alloy, the first crystallization stage consists of two steps. During the seemingly simultaneous formation of several crystal formation fcc-Co crystals are formed sequentially. All the results obtained indicate heterogeneous nanocrystal formation with the nucleation on structurally related ordered regions (on ordered clusters which consist of alloy components with the structure related to the crystallizing phase).

### 1. Introduction

Amorphous and composite amorphous-nanocrystalline alloys are among materials with high magnetic and mechanical properties [1-10]. Amorphous alloys are usually produced as ribbons by rapid melt quenching onto a fast-moving substrate. Under subsequent treatment (heat treatment, deformation, irradiation, etc.), a combined amorphous-crystalline structure can be formed. For small-sized crystals (nanocrystals) to be formed under crystallization, the process of crystallization must occur at a high rate of crystal nucleation and low rate of crystal growth. For the first time, this process has been carried out in an amorphous alloy of Fe-Si-B system which was alloyed with Cu and Nb. To provide the high rate of crystal nucleation and low rate of crystal growth, 1 at.% Cu and 3 at.% Nb were added to an alloy of Fe-Si-B base composition: Cu clusters were the places of the facilitated nucleation of crystals, and slowly diffusing Nb provided the low rate of their growth. The first amorphous-nanocrystalline alloy produced in this way was named Finemet [11–14]. Later on, this approach was used to produce nanocrystalline alloys with different compositions [15-17]. It is important to note that when nanocrystals nucleate on Cu clusters, these clusters are only the places of facilitated nucleation; they are not related structurally to crystals being formed. Cu has an fcc lattice, and Fe-based crystals being formed have a bcc lattice. That is, Cu clusters are ordered regions with fcc short-range order, and the phase formed under crystallization has bcc short-range order. Consequently, crystal nucleation on Cu clusters reflects a difference in the energy gain under heterogeneous nucleation as compared with homogeneous crystal nucleation in the bulk of an amorphous matrix.

However, another mechanism of nanocrystal formation is also possible. One can assume that ordered regions with the short-range order corresponding to that of the phase formed under crystallization are the places of nanocrystal nucleation. When components are distributed non-uniformly in regions enriched with an alloying element, the formation of an ordered structure is possible. The presence of certain orientation ratios between the lattice of an alloying element and that of the formed crystalline phase may promote an increase in the number of potential places of nanocrystal nucleation. This idea is based on a number of prerequisites. As is well-known, short-range order in the amorphous phase can change depending on the composition [18,19] or with a change in the temperature [20,21]. In most cases, at the initial stage of amorphous alloy crystallization crystalline phases are formed which have the structure and composition close to the short-range order and composition of the amorphous phase immediately before crystallization start ("inheritance" of the structure) [22]. In most cases, these phases are metastable [22–25]. These phases generally have a structure similar to that of the basic alloy component. When investigating

https://doi.org/10.1016/j.jnoncrysol.2021.120864

Received 1 March 2021; Received in revised form 5 April 2021; Accepted 7 April 2021 Available online 14 April 2021 0022-3093/© 2021 Elsevier B.V. All rights reserved.

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amorphous alloys of Ni-Mo-B and Ni-Mo-P systems, it was found that under the separation of the amorphous phase (the formation of nanoglass or a heterogeneous amorphous structure consisting of several amorphous phases) each of the amorphous regions is crystallized independently of one another with the formation of "its own" crystalline phase [26]. It was found in [27] that the parameters of a nanostructure (nanocrystal size and the fraction of the nanocrystalline phase) depend on whether nanocrystals are formed in the homogeneous or heterogeneous amorphous phase. All this agrees with the assumption of the action of the mechanism above: nanocrystal nucleation on ordered regions with the short-range order corresponding to that of the crystalline phase being formed.

The present work focuses on the study of the possibility of the formation of nanocrystals with a crystal lattice related to that of an alloying component and different from that of the basic alloy component. For this to be done, amorphous alloys of Co-Fe-B system alloyed with Nb or Ti (elements with a bcc and hcp lattice, respectively) were selected. The reason for the choice of these alloys is also that these materials are characterized by high Curie temperature, and relatively high saturation induction is preserved when the temperature increases. This allows using their magnetic properties at elevated temperatures.

### 2. Experimentals

 $(Co_xFe_y)Nb_8B_{20}\,$  and  $(Co_xFe_y)Ti_8B_{20}\,$  amorphous alloys were produced as ribbons by rapid melt quenching. The cooling rate was  $\sim 10^6$  K/s. The width of the produced ribbons was about 1 cm, and the thickness was  $\sim 40~\mu m$ . The composition of the alloys was monitored using local X-ray microanalysis by means of a Zeiss Supra 50VP scanning electron microscope (Carl Zeiss, Germany,  $\pm$  1 nm).

After the production, the alloys were subjected to isothermal annealing and heating at a constant rate. The isothermal annealing was performed at 400-700°C for different time periods in a resistance furnace. The heating was performed at a constant rate (20°C/min) in a differential scanning calorimeter (Perkin-Elmer DSC-7, USA,  $\pm$  1°). The structure of initial and treated samples was studied by X-ray diffraction analysis and transmission electron microscopy (JEOL, Japan). The X-ray diffraction studies were carried out by means of a X-ray diffractometer (Siemens D-500, Germany) using Co K<sub>\alpha</sub>-radiation with scan step 0.05°. When processing the spectra, special programs were used that allow smoothing and correcting the background. The penetration depth of X-ray beams was calculated by the formula:

$$I = I_0 \exp(-\mu t)$$

where  $I_0$  is the intensity of X-ray beams falling onto a sample, *t* is the distance which is covered by beams in a sample, and  $\mu$  is the absorption coefficient of X-ray beams [28]. The samples for electron microscope studies were prepared by ion thinning. The size of the formed nanocrystals was determined by X-ray diffraction patterns using the Selya-kov–Scherrer formula [29] and by dark-field electron microscope images.

### 3. Results

After the quenching, the samples were amorphous. No signs of the crystalline phases were observed in the X-ray diffraction patterns and electron microscope images. When heating to temperatures below 450°C, no structural changes occur. Fig. 1 shows the thermograms (DSC curves) of the samples of  $Co_{56}Fe_{16}B_{20}Nb_8$  and  $Co_{56}Fe_{16}B_{20}Ti_8$  alloys (curve 1 and 2 respectively). For clarity, the curves are displaced relative to each other along ordinate axes. Crystallization starts at 490°C in  $Co_{56}Fe_{16}B_{20}Nb_8$  alloy and  $460^{\circ}C$  in  $Co_{56}Fe_{16}B_{20}Ti_8$  alloy.

The DSC curves for both alloys look very similar. However, the structure formed at an initial crystallization stage is markedly different. Fig. 2 illustrates the X-ray diffraction pattern of  $Co_{56}Fe_{16}B_{20}Nb_8$  alloy



Fig. 1. DSC curve for  $Co_{56}Fe_{16}B_{20}Nb_8$  (1) and  $Co_{56}Fe_{16}B_{20}Ti_8$  (2) alloys (heating rate of  $20^\circ C/min$ ).



Fig. 2. X-ray diffraction pattern of  $Co_{56}Fe_{16}B_{20}Nb_8$  alloy after the first stage of crystallization.

after the completion of the first crystallization stage. One can see that at the initial stage of the crystallization of Co<sub>56</sub>Fe<sub>16</sub>B<sub>20</sub>Nb<sub>8</sub> amorphous alloy, the crystalline phase with a bcc lattice with space group Im3m with a lattice parameter of 2.835±0.002 Å (the indices of hkl reflections from the bcc structure are marked in the figure) is formed. The structure formed at an early crystallization stage depends on the chemical composition of an alloy. The fraction of the bcc phase decreases significantly with a change in the concentration of alloy components having a bcc structure. Fig. 3 shows the X-ray diffraction patterns of Co<sub>100-</sub> <sub>x</sub>Fe<sub>x</sub>B<sub>20</sub>Nb<sub>8</sub> alloys containing 5, 10, and 16 at.% Fe. The reflections corresponding to the bcc phase are marked with crosses. When the concentration of the components with a bcc lattice (Fe + Nb) decreases, the fraction of the fcc phase decreases. When the content of the bcc component is less than  $\sim$ 13 at.% (5 at.% Fe + 8 at.% Nb), no reflections from the bcc phase are observed in the X-ray diffraction pattern. An average nanocrystal size in the alloys depends on Fe concentration: when it increases, an average nanocrystal size decreases from  $\sim 50$  to ~12 nm.

In contrast to the alloy with Nb, several crystalline phases are formed



Fig. 3. X-ray diffraction patterns of annealed Co56Fe16Nb8B20 (1),  $Co_{62}Fe_{10}Nb_8B_{20}$  (2) and  $Co_{67}Fe_5Nb_8B_{20}$  (3) alloys.

at the first crystallization stage of the alloy with Ti. Fig. 4 demonstrates the X-ray diffraction pattern of annealed Co<sub>56</sub>Fe<sub>16</sub>B<sub>20</sub>Ti<sub>8</sub> alloy. Fig. 5 illustrates the region of the most intense reflections of the X-ray diffraction pattern demonstrated in Fig. 4. The analysis of the X-ray diffraction patterns shows that the crystallization of this alloy results in the formation of Co<sub>23</sub>B<sub>6</sub>-type phase (fcc lattice with space group Fm3m, the lattice parameter is 10.550±0.002 Å, fcc Co, Co<sub>3</sub>B phase (orthorhombic lattice with space group Pnma), and a small quantity of the bcc phase. It is important to note that the most intense line (110) of the bcc phase coincides with the most intense line (031) of Co<sub>3</sub>B phase. As follows from the figure, there are other overlapping lines. Although some of the lines in the X-ray diffraction pattern overlap each other, the analysis with respect to the intensities and half-widths of diffraction lines indicates that all the mentioned phases are present in the sample. In Fig. 4, the reflections from the phases are marked with asterisks (bcc phase), crosses (Co<sub>23</sub>B<sub>6</sub>), circles (fcc-Co), and arrows (Co<sub>3</sub>B).

Thus, in  ${\rm Co}_{56}{\rm Fe}_{16}B_{20}M_8$  (M = Nb or Ti) alloys the structure of the phase formed under crystallization depends on that of an alloying



Fig. 4. X-ray diffraction pattern of  $\rm Co_{56}Fe_{16}B_{20}Ti_8$  alloy after the first stage of crystallization.



Fig. 5. Part of the X-ray diffraction pattern shown in Fig. 5.

component.

Since it is well-known that under the crystallization of amorphous alloys the structure of subsurface and distant from the surface layers of a sample can be different [30,31], the depth of X-ray beam penetration (the thickness of a layer from which information is obtained during X-ray diffraction studies) was determined for each of the alloys. The calculated depth of X-ray beam penetration in the region of the first diffuse maximum and the most intense diffraction maxima is  ${\sim}9.5\,\mu m$  in  $Co_{56}Fe_{16}Nb_8B_{20}$  alloy and  ${\sim}10.3\,\mu m$  in  $Co_{56}Fe_{16}Ti_8B_{20}$  alloy. From the viewpoint of the determination of phase composition, these values can be regarded as approximately equal.

Samples with equal fractions of the crystalline phase were prepared for the electron microscope study. For this to be done, initial amorphous samples were heated in the calorimeter to temperatures corresponding to the same transformation degree (465 and 495°C, respectively) and quickly cooled down. After this treatment, foils were prepared for the electron microscope study. The samples were thinned by ion polishing. At that, the temperature of the sample was monitored to avoid heating of the samples during the thinning. Figs. 6 and 7 show the microstructure of  $Co_{56}Fe_{16}Nb_8B_{20}$  (Fig. 6) and  $Co_{56}Fe_{16}Ti_8B_{20}$  (Fig. 7) alloys, which is formed at an initial crystallization stage. An average nanocrystal size determined by the images is markedly different and is 4 nm in the alloy with Ti and 2 nm in the alloy with Nb. Figs. 8 and 9 demonstrate the size



Fig. 6. TEM image of  $Co_{56}Fe_{16}Nb_8B_{20}$  alloy.



Fig. 7. TEM image of  $Co_{56}Fe_{16}Ti_{8}B_{20}$  alloy.



Fig. 8. Size distribution of nanocrystals in Co<sub>56</sub>Fe<sub>16</sub>B<sub>20</sub>Nb<sub>8</sub> alloy.



Fig. 9. Size distribution of nanocrystals in Co<sub>56</sub>Fe<sub>16</sub>B<sub>20</sub>Ti<sub>8</sub> alloy.

distributions of nanocrystals for the investigated samples. In the case of  $Co_{56}Fe_{16}B_{20}Nb_8$  alloy (Fig. 8), the distribution is quite narrow. For  $Co_{56}Fe_{16}Ti_8B_{20}$  alloy (Fig. 9) the distribution is significantly wider. This may reflect the contribution of nanocrystals of different crystalline phases.

It is important to note the following. Figs. 4 and 5 show the X-ray diffraction patterns of Co<sub>56</sub>Fe<sub>16</sub>B<sub>20</sub>Ti<sub>8</sub> alloy after the completion of the first crystallization stage. The X-ray diffraction patterns of the samples obtained after heating in the calorimeter to the temperature of the completion of the first crystallization stage and after isothermal annealing in the furnace look similar. The results of the X-ray diffraction analysis show that after the completion of the first crystallization stage the samples are multiphase. However, the results of the electron microscope studies of the structure of foils prepared after sample heating to temperatures corresponding to the very crystallization start indicate the presence of only bcc crystalline phase. Phase formation under crystallization apparently begins not simultaneously, and the maximum in the DSC curve is the superposition of two (or more) closely spaced peaks. In this case, the crystallization process seems to be the simultaneous formation of several crystalline phases which, in fact, start to be formed not simultaneously.

### 4. Discussion

As was shown above, a crystalline structure formed at an initial crystallization stage depends on the alloy composition. One could expect that the crystallization of alloys would start with the precipitation of Co crystals, a Co-based solid solution, or Co borides, as in the case of the crystallization of alloys of Co-B, Co-Si-B system [32-34]. Thus, for example, it was shown in [32] that under the crystallization of  $Co_{77}Si_{11.5}B_{11.5}$  alloy  $\alpha$ -Co is formed; at later crystallization stages,  $Co_2B$ and Co3B borides and Co2Si silicide precipitate from the residual amorphous matrix. In the case of multicomponent alloys, the simultaneous formation of Co crystals of different modifications, as well as boride and silicide phases, may occur:  $\alpha$ -Co, Co<sub>2</sub>B, and  $\beta$ -Co<sub>2</sub>Si or  $\alpha$ -Co, Co<sub>2</sub>B, β-Co<sub>2</sub>Si, and (Fe,Co)<sub>3</sub>Si phases are formed in alloys of Co-Si-B-Cr system depending on the composition [33]. It was found later that under the crystallization of a Co-based amorphous alloy alloyed with Fe, the formation of the bcc phase is possible in a concentration range in which, according to the phase diagram, it should not be formed [35]. At that, it was determined [35] that the presence of bcc components in the amorphous phase is necessary for the formation of the bcc phase. It was also found that the parameters of a structure formed under crystallization depend significantly on the concentration of bcc components: when it increases, the size of nanocrystals decreases, and their fraction increases.

The results above agree with the results obtained in [35]. Fig 3 shows that the fraction of the nanocrystalline phase increases with an increase in the Fe concentration. One might assume that the formation of the bcc phase is determined only by Fe concentration. However, it was found earlier [36] that in alloys of Co-Si-B-Fe-Nb system the bcc phase is formed neither at low Fe content nor in the absence of Nb. It was shown that for the formation of this phase the concentration of bcc components (Fe + Nb) should be higher than some "critical" value; at that, the presence of both components is necessary in some cases. It was assumed in [36] that when Co-based alloys are alloyed with Fe and Nb, the formation of the bcc phase in them may be caused by the relationship between the structures of alloying components (1) and by the presence of equal interplanar spacings (2) some of which coincide with the interplanar spacings of a phase formed under crystallization. Indeed, in the alloys under study Nb and Fe have an equal lattice with space group Im3m, and several coincident interplanar spacings are observed, for example,  $(d_{(220)Nb} = 1.169 \text{ Å} \text{ and } d_{(211)Fe} = 1.167 \text{ Å})$  or  $(d_{(310)Nb} = 1.045 \text{ }$  ${\rm \check{A}}=d_{(220)bcc}$ ). The formation and growth of nanocrystals with a bcc lattice can occur on the surface of an ordered region (cluster) with the short-range order characteristic of a bcc lattice. The lattice parameter of the formed bcc phase (2.835 Å) differs by that of  $\alpha$ -Fe (2.866 Å) by about 1%. At this difference between lattice parameters, the epitaxial growth of nanocrystals on ordered regions is possible. In this case, the process of heteroepitaxy, i.e., oriented growth of a crystal that differs in composition from a cluster on which the growth occurs, can take place. Thus, when ordered regions are formed, the epitaxial growth of nanocrystals on these ordered regions is possible due to the alloying with bcc elements (Fe, Nb). If an amorphous structure contains ordered regions, these regions will be the places of facilitated crystal nucleation.

The addition of elements with a bcc lattice to an alloy, the basic component of which has an fcc or hcp lattice, is important for the following reason. It was shown in [18,19] that even a very small change in the chemical composition can lead to a change in the short-range order of an amorphous phase structure. Thus, for example, when investigating the structure of  $(Zr_{0.667}Ni_{0.333})_{1-x}B_x$  amorphous alloy with B content between 0 and 25 at. % it was found that at  $x \approx 0.05$  the type of short-range order changes [37]. Therefore, in the case of even small inhomogeneities in the amorphous phase, it contains regions that differ from the matrix in composition (and type of short-range order). If these regions have short-range order similar to that of a phase being crystallized, the probability of the formation of this phase increases. The presence of these regions in the amorphous phase was found in alloys with different compositions [22,38–40].

In the light of the foregoing, the dependence of the formation of the bcc phase on the concentration of components with a bcc lattice is also clear. The higher the content of these components is, the more regions enriched with them are present in the amorphous phase and, therefore, the more places of the potential nucleation of nanocrystals with the same lattice are. This makes the alloys under study different from alloys of Finement group in which the number of the places of heterogeneous nucleation is limited by Cu concentration (1 at. %). Nanocrystal nucleation on ordered regions implies the presence of regions that differ from the basic amorphous phase. A heterogeneous amorphous structure contains regions that differ from the matrix in composition (and type of short-range order). As stated above, the fraction of the nanocrystalline phase depends on the state of an amorphous matrix before crystallization start. It was shown in [27] that the fraction of nanocrystals formed in a heterogeneous amorphous structure is higher than that of nanocrystals formed in the homogeneous amorphous phase. This also indicates a larger number of potential nucleation places in an amorphous structure containing clusters.

In contrast to Fe and Nb, Ti has an hcp lattice with space group P6<sub>3</sub>/ mmc (with the parameters a = 2.95 Å, c = 4.682 Å). It does not contain structural elements that coincide with a bcc lattice. Therefore, it is natural that when Fe and Nb are replaced by Ti, no nanocrystals with a bcc lattice are formed; when Fe and Nb are partially replaced by Ti (in the presence of Fe), their fraction decreases significantly (Figs. 3 and 4). These results support the assumption of nanocrystal nucleation on "prepared" ordered regions. The formation of the bcc phase in  $Co_{56}Fe_{16}B_{20}Ti_8$  alloy is obviously due to quite a high Fe concentration. With this Fe content (16 at.%), the amorphous phase may also contain ordered regions enriched with Fe with fcc-type short-range order. If these regions are the places of facilitated nanocrystal nucleation, as discussed above, the formation of nanocrystals will begin earlier in these places. A difference in the microstructure at initial devitrification stages (TEM study) and after the completion of the first crystallization stage (Xray study) confirms this assumption. As stated above, during the seemingly simultaneous formation of several crystalline phases in Co<sub>56</sub>Fe<sub>16</sub>B<sub>20</sub>Ti<sub>8</sub> alloy, phases with different chemical compositions and different crystal lattices are formed sequentially.

The comparison of the microstructure of  $Co_{56}Fe_{16}B_{20}Nb_8$  and  $Co_{56}Fe_{16}B_{20}Ti_8$  alloys heated to temperatures corresponding to the same transformation degree demonstrates that in the alloy with Nb nanocrystal size is less than that in the alloy with Ti. If nanocrystals nucleate on ordered regions with bcc-structure-type short-range order, the number of these regions in  $Co_{56}Fe_{16}B_{20}Nb_8$  alloy should be larger. This

means the nucleation of a larger number of bcc nanocrystals in this alloy. This leads to a smaller nanocrystal size (at an equal fraction of the nanocrystalline phase), which is observed experimentally (Figs. 6, 8)

Note that Nb can be not only an element that promotes an increase in the nanocrystal nucleation rate. As is well-known, in Finemet-type alloys it promotes a decrease in the growth rate since it is characterized by a low diffusion coefficient [41]. In principle, Nb can play the same role in the alloys investigated. On the one hand, ordered Nb regions are the places of facilitated nucleation on which nanocrystals with the corresponding orientation ratios of lattices nucleate. On the other hand, nanocrystallization occurs by the primary crystallization mechanism at which the chemical composition of nanocrystals differs from that of an amorphous matrix. This means that when a crystal is growing, Nb should be removed from the reaction front, and it naturally should decelerate the process of crystal growth at a low diffusion coefficient.

The question of nanocrystal formation by the heterogeneous nucleation mechanism is discussed in literature [42,43]. The question of nucleation centers and their nature is still open. It was assumed in [41] that in Al alloys containing a rare-earth component, places depleted in the rare-earth component are the centers of nanocrystal nucleation. Alloys of Al-TM-RE system (TM is a transition metal, RE is a rare-earth metal) were extensively investigated [44-48]. The results obtained (for example, [43]) confirmed the assumption suggested in [42].

If the mechanism of crystal nucleation discussed above is correct, there should be fewer potential places of crystal nucleation in the alloy with Ti. Correspondingly, in the alloy with Nb there are more of these places, and a crystal size turns to be smaller. The amorphous phase is thermodynamically unstable, and in the simplest case of homogeneous nucleation (without taking into account deformation contribution) the size R<sub>c</sub> of a critical nucleus under the phase transition to a stable state (crystallization) will be determined by the formula  $R_c = 2\sigma/\Delta F$  where  $\sigma$ is the specific energy of the nanocrystal-amorphous phase interface, and  $\Delta F$  is the difference between the free energies of volume units of the amorphous and crystalline phases. As stated above, the crystallization temperature of the alloy with Nb is 30°C higher than that of the alloy with Ti. Consequently, the value of free energy for this alloy is less than that for the alloy with Ti. Therefore, the thermodynamic stimulus of a phase transition ( $\Delta F$ ) will be less, too. It was shown above that an average nanocrystal size is 2 nm in the alloy with Nb and 4 nm in the alloy with Ti. At this average size and the same fraction of the crystalline phase, the number of nucleation centers (it corresponds to the number of nanocrystals) differs by approximately 8 times. Thus, the data obtained indicate nanocrystal formation by the heterogeneous mechanism. At that, the presence of regions with a relative crystal lattice is the reason for bcc phase formation.

Note that in the case under consideration, nanocrystals can be formed not by the primary crystallization mechanism; polymorphouscrystallization-type processes can take place in local regions. As mentioned above, when a heterogeneous amorphous structure consisting of regions with different chemical compositions and different shortrange orders is formed, crystallization results in the formation of the "own" crystalline phase in each of these regions [26]. In this inhomogeneous amorphous structure, a crystalline phase is formed in each region which is characterized by the same composition and type of short-range order as an amorphous region where this phase nucleates and grows. It was indicated in [26] that an apparent crystallization mechanism changes at that. Instead of eutectic crystallization (simultaneous formation of several crystalline phases that is accompanied by diffusion redistribution of components at distances that are significantly larger than the interatomic ones), the simultaneous polymorphous crystallization (without a significant change in the composition) of many different amorphous regions of a heterogeneous structure occurs.

If one compares the processes of nanocrystal formation in alloys of the Finemet group and in the investigated alloys, the following should be highlighted. In Finemet-type alloys, Cu clusters are only the regions of facilitated nucleation; they are not related structurally to nucleating

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crystals. Crystal nucleation on Cu clusters reflects the energy gain under heterogeneous crystal nucleation on some cluster (inhomogeneity) as compared to homogeneous crystal nucleation in the bulk of an amorphous matrix. In the alloys investigated above, nanocrystal nucleation is also heterogeneous. However, the presence of certain orientation ratios between the lattice of an alloying element and that of the formed crystalline phase (nanocrystal nucleation on structurally related ordered regions) facilitates nanocrystal nucleation.

Strictly speaking, when analyzing crystallization processes one should consider at least two "parameters": the relationship between the crystal lattices of alloy components (1) and the effect of an alloying element on the widening of the region of bcc phase existence (2). In the first case, the heterogeneous nucleation of the bcc phase will occur on the clusters of alloy components with a relative crystalline structure; at that, the crystallization process will be determined by the surface energy. In the second case, the phase composition will depend on the total dependence of free system energy on the chemical composition ("volume" free energy), but not only on the easiness of the implementation of a certain mechanism and specifics of nanostructures in which the fraction of surface energy is high. As is well-known, the phase diagrams of Co-Fe system [49] contain the regions of bcc phase existence. Drawing an analogy with the effect of alloving components on the region of α-phase existence in steels, one should expect that both alloying components will promote the widening of this region. In this regard, their effect on the possibility of the formation of a bcc phase is the same. Therefore, the data obtained indicate an undeniable effect of the first factor. However, further studies are necessary for a final conclusion.

#### 5. Conclusion

As a result of the studies carried out, it has been determined that the alloying of amorphous alloys of Co-Fe-B system with elements having a bcc lattice promotes the formation of a metastable phase with this lattice during crystallization. Nanocrystal size and the fraction of the phase with a bcc lattice depend on the concentration of alloying components with this lattice. When the concentration of bcc components increases, nanocrystal size decreases. When Nb (an element with a bcc lattice) is replaced by Ti (an element with an hcp lattice), the fraction of the bcc phase decreases, and multiphase crystallization (simultaneous formation of several crystalline phases) occurs. In Co<sub>56</sub>Fe<sub>16</sub>B<sub>20</sub>Ti<sub>8</sub> alloy, the first crystallization stage consists of two steps: first the formation of a small quantity of the bcc phase and then the formation of Co<sub>23</sub>B<sub>6</sub> and fcc-Co crystals. That is, during the seemingly simultaneous formation of several crystalline phases, phases with different chemical compositions and different crystal lattices are formed sequentially. All the results obtained indicate heterogeneous nanocrystal formation with the nucleation on structurally related ordered regions (on ordered clusters which consist of alloy components with the structure related to the crystallizing phase).

#### CRediT authorship contribution statement

G.E. Abrosimova: Methodology, Writing – original draft. N.A. Volkov: Data curtion, Software. E.A. Pershina: Visualization, Validation. V.V. Chirkova: Investigation. I.A. Sholin: Investigation. A.S. Aronin: Supervision, Writing - review & editing.

#### **Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Acknowledgements

The research is carried out within the state task of ISSP RAS and

partially supported by the RFBR (grant no. 19-02-00406).

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