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Structural changes of $\text{Co}_{70}\text{Fe}_5\text{Si}_{10}\text{B}_{15}$ amorphous alloy induced during heating

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Abstract

In this study we present the results on complex structural changes of the $\text{Co}_{70}\text{Fe}_5\text{Si}_{10}\text{B}_{15}$ amorphous alloy induced during heating in the temperature range between 20 and 1000 °C. The structural and phase transformation changes were correlated with DTA, XRD and SEM properties. It is shown that initial $\text{Co}_{70}\text{Fe}_5\text{Si}_{10}\text{B}_{15}$ alloy during heating undergoes complex crystallochemical changes. In the range between ambient temperature and near 400 °C, investigated alloy retains the solid-state amorphous properties. Prolonged heating induces complete transformation to crystalline solid state. The solid–solid amorphous to crystalline state transformation process is completed at 500 °C, when two nanocrystalline phase alloy systems are formed. Prolonged thermal treatment between 600 and 1000 °C, influenced further elemental segregation and phase transition. At 1000 °C, the composite material consisting of two FCC cobalt-rich alloys and a hexagonal unidentified alloy are formed.

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1. Introduction

The amorphous metallic alloys represent a class of materials characterized by structure with absence of the long-range order [1,2]. For multi-component alloys this is more universal feature. As the first approach, amorphous alloys can be considered as two or multi-components solid solutions, like a liquid solutions. However, they possess the typical properties of solids. According to intensive experimental investigations, the amorphous alloys can be obtained practically in any multi-component system. There are several methods developed for preparation this class of materials. They are based on rapid cooling of liquid metals, alloys or their vapors condensing on a cold support and other methods used for achieving strong non-equilibrium conditions [3,4]. Synthesized alloys in forms of ribbon or wire represent a new materials with an interesting combination of physical prop-

erties that make them very attractive from the technical point of view.

The amorphous state of matter is, however, structurally and thermodynamically unstable and very susceptible to partial or complete crystallization during thermal treatment or non-isothermal compacting. The latter imposes the knowledge of alloys stability in a broad temperature range due to different crystallization processes [5], which appears during heating. However, by annealing below the crystallization temperature this material undergoes structural relaxation processes including two competitive processes: free volume decrease, which lowers the rate of diffusion mass transport, and arranging process which brings the alloy closer to the crystalline state by increasing its readiness for crystallization. Physical features of amorphous metal alloys are irreversibly changed in the process of structural relaxation occurring slightly below the crystallization temperature. Kinetic properties of amorphous alloys show a correlation between the physical nature of anomalous behavior of electronic states density at the Fermi level, thermal conductivity, heat capacitance and electrical resistivity and structural inhomogeneities in these materials.

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Recently, a giant magnetoimpedance (GMI) effect, discovered in the amorphous alloys, has generated growing interest among researchers and manufacturers because of their practical use for magnetic sensing and recording applications [6–9]. Among these alloys, those from the quaternary Co–Fe–Si–B system have attracted considerable attention in recent years [7–12]. However, the physical properties of this amorphous alloy systems are strongly dependent on composition, the cooling rate, oblique of alloy, subsequent thermal treatment, etc.

Our recent published results on $\text{Co}_{84}\text{Fe}_5\text{Si}_{8.5}\text{B}_{2.5}$ amorphous alloy [13] show that crystallization occurs via three steps. The first two steps, nucleation and formation of microcrystallites between 530 and 540 °C are insufficient to give measurable XRD changes. The real crystallization process takes place during the last step at temperatures above 800 °C. Our results obtained on $\text{Co}_{70}\text{Fe}_5\text{Si}_{10}\text{B}_{15}$ amorphous alloy by measuring the thermo-electromotive force during isothermal annealing at temperatures under crystallization point [14] show influence of the change free electron state density at the Fermi level on electrical and magnetic properties of investigated alloy.

To explain the mentioned influences, in this study, we investigated the thermal stability and structural transformations of $\text{Co}_{70}\text{Fe}_5\text{Si}_{10}\text{B}_{15}$ amorphous alloy in broad interval from ambient temperature to 1000 °C.

2. Experimental procedure

A 30- μm thick ribbon of the $\text{Co}_{70}\text{Fe}_5\text{Si}_{10}\text{B}_{15}$ amorphous alloy, prepared in the Baykov Institute of Metallurgy in Moscow by the melt spinning method, was used as a sample in our research.

The thermal stability was investigated by non-isothermal analysis (DSC) using a Du Pont Thermal Analyzer (model 1090). In this case, samples of about several milligrams were heated in the DSC cell from room temperature to 700 °C, at heating rates of 5, 10, 15, 20 and 40 °C/min, in a stream of nitrogen at ambient pressure.

The X-ray powder diffraction (XRD) patterns were recorded on a Philips PW-1710 automated diffractometer using a Cu tube operated at 40 kV and 30 mA. The instrument was equipped with a diffracted beam curved graphite monochromator and Xe-filled proportional counter. For routine characterization diffraction data were collected in the 4–100° 2θ range of Bragg angles, counting for 1 s. Diffraction data for a crystallite size measurements between 40° and 50° Bragg angles were collected using a 4 s scan at 0.02° steps. A fixed 1° divergence and 0.1 mm receiving slits were used. Silicon powder was used as an external standard for calibration of diffractometer. All XRD measurements were recorded on a solid samples in a form of ribbon at ambient temperature. Prior to XRD experiment the samples were heated to the elevated temperatures for 20 min in the nitrogen atmosphere.

The unit cell dimensions of alloys formed at 1000 °C were calculated from powder data by least-square refinement procedure using program Lsucricp [15]. The face centered cubic unit cell dimensions and $Fm\bar{3}m$ space group for Co found in JCPDF data base (file card 15-0806), were applied as a starting parameters for least-square procedure. Crystallite size dimensions, i.e. the length of coherent ordered structure ($\langle D_{hkl} \rangle$ Å), were determined by using an interactive Windows program for profile fitting and size analysis Winfit [16]. Full-width at half-maximum (FWHM) values of the (1 1 1) peaks at Bragg angle $2\theta = 44.9^\circ$, were fitted assuming a Pearson VII function for a profile.

The microstructure and composition homogeneity of the obtained samples were investigated by a scanning electron microscope JOEL-JSM 5300. Prior to the microscope observation Au thin film was applied on flat surfaces of the specimens.

3. Results and discussion

3.1. Thermal investigations

To estimate the ability of alloys to form amorphous phases and to define their thermal stability the kinetics of crystallization during heating is usually investigated. For this purpose thermal analysis is the most frequently used methods [17]. Using different heating rates and measuring one property, proportionally connected with the degree of conversion, the dependence of conversion rate on temperature and time can be determined. The general equation enabling the analysis of conversion kinetics for nucleation and growth of particles of new phase was proposed by Avrami [18]:

$$\xi(\tau) = 1 - \exp[-(k\tau)^n] \quad (1)$$

where $k = k_0 \exp(-E_a/RT)$ and $\xi(\tau)$, n , k_0 , E_a are degree of transformed, Avrami constant volume, frequency factor and activation energy, respectively.

From this equation by using various approaches for the transition to constant rates of heating β_i and by checking the characteristic temperatures T_i corresponding to the definite part of conversion (ξ), we can obtain expressions for calculation of activation energy of processes known as Ozawa's equation [19]:

$$\ln \beta = -\frac{E_a}{RT_i} + C_1 \quad (2)$$

and Kissinger's equation [20]:

$$\ln \left(\frac{T_i^2}{\beta_i} \right) = \frac{E_a}{RT_i} + C_2 \quad (3)$$

where C_1 and C_2 are constants.

The linearity criterion of the experimental data plotted in the corresponding coordinates is usually taken as a proof of reliability of one or another equation.

According to DSC measurements (Fig. 1), the alloy crystallizes step by step with two well formed exothermic maxima at temperatures at about $T_1 = 460$ °C and $T_2 = 540$ °C, respectively. However, it is important to notice here that discussed thermally

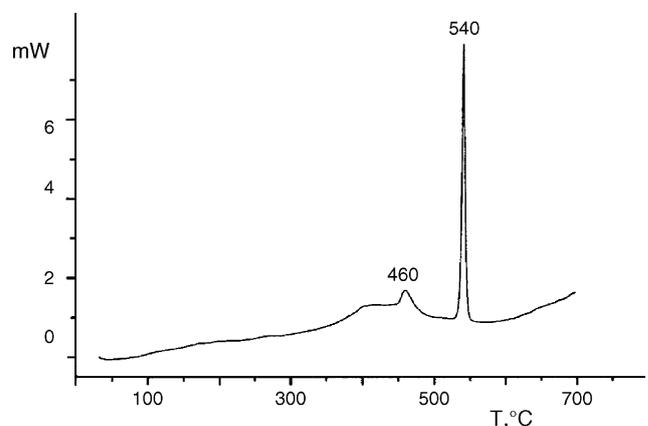


Fig. 1. DSC curve of initial amorphous $\text{Co}_{70}\text{Fe}_5\text{Si}_{10}\text{B}_{15}$ alloy; heating rate 10 °C/min.

Table 1

The thermal and kinetic parameters process of crystallization

Step	E_a (Kissinger) (kJ/mol)	E_a (Ozawa) (kJ/mol)	k (s ⁻¹)	$t_{1/2}$ (s)
1	433.1 ± 11	445.5 ± 11	0.019	36.5
2	543.5 ± 11	554.9 ± 11	0.023	30.1

induced changes, i.e. crystallization processes, already started earlier at 400 °C, which is confirmed by XRD experiment. The thermal and kinetic values of the crystallization process were determined by analyzing the shifts of exothermal maxima in DSC thermograms depending on the heating rate (Table 1). The activation energies of both crystallization steps were determined according to Eqs. (2) and (3). The process frequency factors were determined according to relation $k_0 = [\beta E \exp(E/RT)]/RT^2$. From the relation $k = k_0 \exp(-E/RT)$, the crystallization rate constants were determined for temperature of the exothermal maxima. The error of calculating of activation energies was determined as a root-mean-square deviation multiplied on Student's coefficient for the probability 0.95.

It is interesting to note the high values of the calculated activation energies of amorphous alloy crystallization processes (Table 1). The activation energy of solid-state reactions proceeding through formation of nuclei and their growth, according to opinion of some researches [17], has no physical meaning but only empirical character and practically establishes only the dependence of the rate of conversion on temperature. This energy can be spent, not only for overcoming the activation barrier but, mainly for its downturn due to cooperative displacement of atoms [21]. Thus in experiments, the total value of energy spent both, for downturning the potential activation barrier and for its overcoming is determined. The opinion that the elementary act of solid-state conversion is accompanied by simultaneous correlated displacement of groups of atoms is especially relevant to the process of crystallization of amorphous alloys, which is well described by the kinetics of viscous flow characterized by the simultaneous movement of atom collectives. Finally, the crystallization of amorphous alloys is a very complicated process accompanied by nucleation and growth of various crystal phases under continuously varied conditions of chemicals

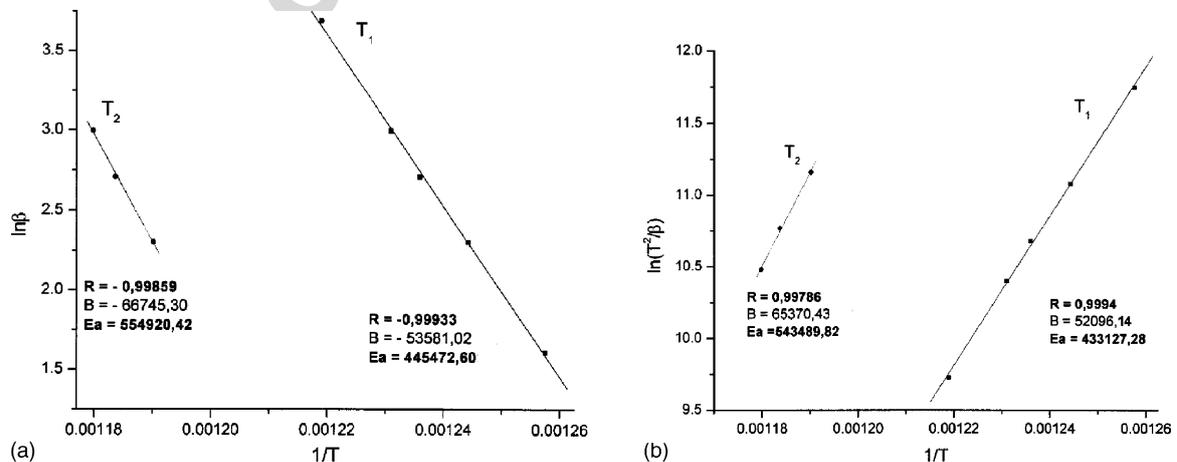
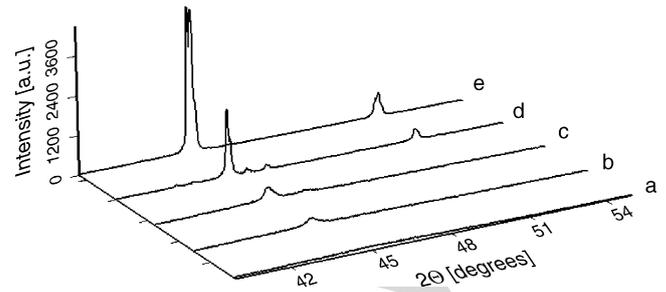
Fig. 2. The activation energy plots: (a) $\ln \beta = f(1/T)$ according Ozawa and (b) $\ln(T^2/\beta) = f(1/T)$ according Kissinger for both steps of crystallization.

Fig. 3. Thermally induced phase evolution of the amorphous $\text{Co}_{70}\text{Fe}_5\text{Si}_{10}\text{B}_{15}$ alloy with temperature increasing: (a) the initial alloy at ambient temperature; (b) the initial alloy heated at 400 °C for 20 min; (c) the initial alloy heated at 500 °C for 20 min; (d) the initial alloy heated at 600 °C for 20 min; (e) the initial alloy heated at 700 °C for 20 min.

surroundings in a zone of conversion. Obviously, such a process occurs not only with the single value of activation energy and not by formation of a single configuration of activated complex [22]. In practice, with the multitude of probable ways of conversions, only those mechanisms and activated complexes of the crystallization process will be realized that are the most probable at a given temperature. Any change of crystallization conditions, such as heating rate, can result in a change of the mechanism and main activation complex of the crystallization process. Thus high values of activation energy of crystallization of amorphous alloys, first of all, indicates that a lot of atoms participate in an elementary act of structure reorganization, as well as high complexity of these processes (Fig. 2).

3.2. X-ray powder diffraction and scanning electron microscopy investigations

The XRD pattern of initial non-heated amorphous $\text{Co}_{70}\text{Fe}_5\text{Si}_{10}\text{B}_{15}$ alloy is shown in Fig. 3 (curve a). The powder patterns obtained after heating of initial alloy at higher temperatures are shown in Fig. 3 (curves b–e).

It is obvious from these figures that initial sample (Fig. 3, curve a), pass through successive phase transformations during heating treatment. Between ambient temperature and 300 °C, initial alloy retains amorphous properties what is consistent with

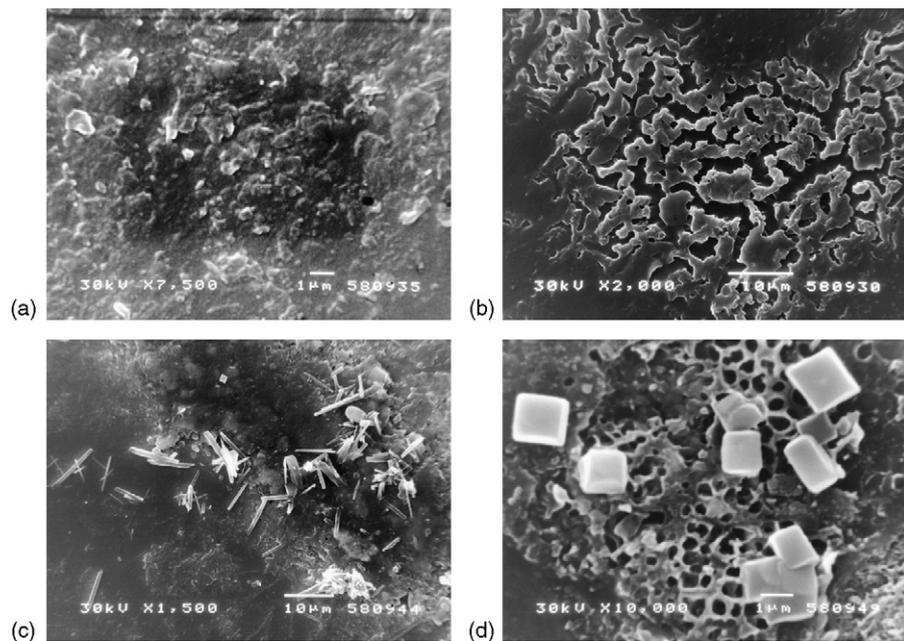


Fig. 4. SEM micrographs of thermally induced phase evolution of amorphous $\text{Co}_{70}\text{Fe}_5\text{Si}_{10}\text{B}_{15}$ alloy: (a) the initial non-heated alloy; (b) the initial alloy heated at 400°C for 20 min; (c) the initial alloy heated at 700°C for 20 min; (d) the initial alloy heated at 1000°C for 20 min.

SEM investigations. A characteristic micrograph obtained from initial alloy is shown in Fig. 4(a). Prolonged heating between 400 and 500°C induces amorphous alloy recrystallization to, at least, two unidentified intermediary crystalline phases (Fig. 3, curves b and c). One of these two phases with characteristic peak at $2\theta = 44.20^\circ$, is more abundant and represent the (1 1 1) interplanar distance of Co-rich FCC cubic crystal lattice. The phase is always present at 400°C (Fig. 4(b)), which means that its crystallization from amorphous matrix started earlier between 300° and 400° . In other words, thermally induced elemental segregation in amorphous ribbon always starts in aforementioned temperature region. The alloy segregation/crystallization processes induced by heating are monitored also by appearance of dendritic forms in SEM micrographs taken between 400° and 500°C . A characteristic micrograph is shown in Fig. 4(b).

Another growing intermediary phase is characterized by appearance of small peak at $2\theta = 45.68^\circ$ (Fig. 3, curve c) which could not be indexed on FCC symmetry. The inspection of JCPDS [23] data base shows that discussed phase is the most similar to Co pattern (file card no. 5-0727) having hexagonal symmetry. It is important to notice that the samples heated at 400 and 500°C are still characterized by presence of considerable quantity of amorphous matter. However, we concluded from grain size measurements that temperature increasing influenced directly growth of Co-rich cubic alloy. This is confirmed by crystallite size measurements at peak $2\theta = 44.20^\circ$. Obtained values of $\langle D_{111} \rangle$ of 125, 165 and 610 \AA for ribbons heated at 400 , 500 and 600°C , respectively; speak in favor of accelerated crystal growth between 400 and 600°C temperature range (Fig. 3, curves b–d). In essence, the observed data can be interpreted in term of crystallochemical changes from nanostructured or strongly disordered to well ordered crystalline state, which have direct influence on physico-chemical characteristics of alloys. It

is readily to notice that crystallite growth coincide with abrupt changes of electrical resistivity [14] and appearance of two exothermal peaks at DSC curve, too (Fig. 1). The extent of heating process complexing and dependence on different parameters clearly show our further considerations. Fig. 3 (curve d) represents powder pattern of $\text{Co}_{70}\text{Fe}_5\text{Si}_{10}\text{B}_{15}$ alloy heated at 600°C . Its basic characteristic is absence of amorphous substance. That means that recrystallization process, i.e. reorganization of initially amorphous alloy into crystalline state is completely finished at 600°C . In the phase composition of alloy obtained at this temperature, the so-called Co-rich FCC phase is quantitatively dominant. Another unidentified crystalline phase, which started to grow between 400 and 500°C , is present in traces (Fig. 3, curves c and d). The phase has the strongest peak at $2\theta = 45.68^\circ$ and its optimal stability conditions correspond to temperature range between 600 and 650°C . This conclusion is supported by phase instability at higher temperatures. Already, upon heating at 700°C , the phase disappeared completely, whereas the FCC Co-rich phase stays stable (Fig. 3, curve e). Another evidence for existence of the unidentified second phase at 600°C we found in SEM micrographs shown in Fig. 4(c), where characteristic elongated prismatic crystals are clearly visible.

Phase analysis of patterns heated between 700 and 1000°C shown in Figs. 3 (curve e) and 5, revealed an interesting order–disorder phenomena connected with dominant Co-rich FCC phase. This is manifested by splitting of all measured peaks in XRD pattern. This unexpected result indicates that FCC Co-rich phase undergoes through additional order–disorder processes. Upon heating at 700°C this is segregated into two FCC Co-rich phases characterized by various cell dimensions like $a_I = 3.5476(5) \text{ \AA}$ and $a_{II} = 3.5384(6) \text{ \AA}$. These results suggest interesting conclusions. If we compare unit cell dimensions mutually and in relation to a FCC pure Co metal ($a = 3.544 \text{ \AA}$,

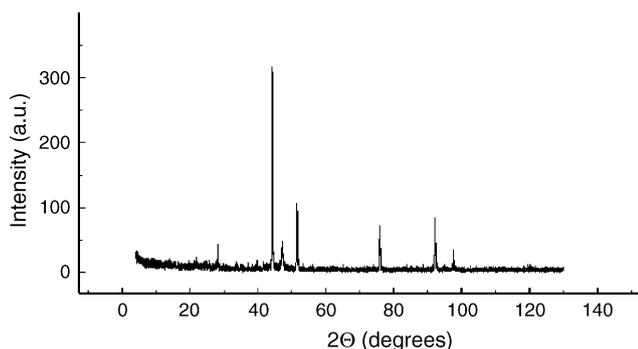


Fig. 5. A whole range XRD powder pattern of $\text{Co}_{70}\text{Fe}_5\text{Si}_{10}\text{B}_{15}$ alloy after heating at $1000\text{ }^\circ\text{C}$ for 20 min.

JCPDS card file no. 15-0806 [23]). It is obvious that FCC Co-rich-I phase has greater (expanded), whereas FCC Co-rich-II phase has smaller (contracted) unit cell in relation to pure Co unit cell. These results undoubtedly speak in favor of Co metal isomorphous replacement by Fe, Si and B atoms and order–disorder phenomena in both segregated alloy phases. Moreover, some of these FCC alloy phases are clearly visible in numerous SEM micrographs obtained between 700 and $1000\text{ }^\circ\text{C}$ as perfect cubic single crystals. A characteristic SEM micrograph taken after heating at $1000\text{ }^\circ\text{C}$ is shown in Fig. 4(d). However, the phase composition of this sample is more complex. The powder pattern (Fig. 5), shows a small presence of third phase with characteristic peak 2θ at $47.20\text{ }^\circ\text{C}$ which is very similar to alloys discussed hexagonal phase.

4. Conclusion

The $\text{Co}_{70}\text{Fe}_5\text{Si}_{10}\text{B}_{15}$ amorphous alloy made by the Baykov Institute of Metallurgy in Moscow was used for thermal characterization in a broad range between ambient temperature and $1000\text{ }^\circ\text{C}$. The results obtained from thermal (DTA, DSC), XRD and SEM measurements allow us to conclude that initial alloy having GMI effect undergoes complex phase transformation processes by heating.

The $\text{Co}_{70}\text{Fe}_5\text{Si}_{10}\text{B}_{15}$ amorphous alloy retains its amorphous structure up to near $400\text{ }^\circ\text{C}$. In that temperature range the electric and GMI magnetic [14] properties remain practically unchanged. Prolonged heating over $400\text{ }^\circ\text{C}$ initiates structural changes of the starting alloy. They are manifested by thermally induced atom interdiffusion accompanied by its elemental segregation and simultaneous crystallization. Grain size XRD measurements show that crystallization processes starts at near $400\text{ }^\circ\text{C}$ with nanosized crystallites. Their growth is temperature dependent. Recrystallization processes between 400 and $500\text{ }^\circ\text{C}$

are very complex and could not be completely resolved. In that temperature range, initial amorphous alloy changed its structural state to completely crystalline which is accompanied by loss of electromagnetic properties. However, in the same temperature range a multiphase crystallization and phase transformation processes start simultaneously. They continue almost up to near $700\text{ }^\circ\text{C}$, where two various FCC Co-rich phases are formed. Its XRD investigations showed that they are quantitatively dominant and stable at $1000\text{ }^\circ\text{C}$. The results of unit cell dimension measurements, indirectly confirm its different chemical composition and final atomic segregation of initial amorphous alloy into a composite material.

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