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Development of high strength thermally stable Al-based alloys with nanocomposite structure

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**14. ABSTRACT**

This report results from a contract tasking Institute for Metal Physics, NAS of Ukraine as follows: The demands on materials set by aerospace and aircraft manufacturers include the development of alloys possessing high strength-to-weight ratios and capable to withstand high temperature exposures during service. One of the promising classes of materials which may meet these requirements are Al-based alloys with nanocomposite structures formed by partial crystallization of amorphous precursors the strength of which may exceed 1500 MPa. Solution of the problems concerning alloys chemistry and ability to tailor of certain microstructures is of prime importance for the development of new nanostructured materials.

The goals of the project are to perform the systematic experimental studies of the effects of alloy composition and thermal prehistory on glass-forming ability, thermal stability, crystallization behaviour and mechanical properties of a series binary, ternary and multicomponent Al-based alloys by transition metals and rare earths as well as to elaborate appropriate theoretical models of nanocrystallization processes. The main factors responsible for nanoscale microstructure formation will be determined from comparison of the experimental data with the model predictions.

As a result a series of new Al-based alloys with nanocomposite structure with improved mechanical properties and enhanced thermal stability will be developed and the fundamental basis for the nanostructured alloys design will be created.

**15. SUBJECT TERMS**
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Development of new high strength bulk structural aluminum alloys with nanocomposite structure

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1. Summary

Studies have been carried out according to the approved technical schedule (Task 2) and the personal executors plans for the second year. At the substage 2.1 experiments on continuous heating of the 12 binary, ternary, quaternary and quinary amorphous Al_{86-90}(Ni,Co,Fe)_{6-8}(Y,Gd,Tb)_{6-10} alloys have been performed and it has been established that crystallization begins at temperatures 440–584 K by formation of the nanocomposite structures (nanocrystals embedded in the residual amorphous matrix) and occurs in the 2 or 3 well-defined stages. The three different nanocrystallization mechanisms of the first crystallization stage have been established including: (1) diffusion limited growth of the quenched-in Al nuclei, (2) nucleation and subsequent diffusion limited growth of Al nanocrystals and (3) nucleation and simultaneous growth of nanoscale crystals of Al and intermetallic compounds (substage 2.1). It has been established (substage 2.3) that formation of nanophase composites having the crystallized volume fractions, the average sizes of Al nanocrystals and the densities in the ranges (0.22–0.59), (14.8–21.0) nm and (1.1–4.3) × 10^{23} m^{-3}, respectively, results in essential increasing of the microhardness (by 740–1740 MPa) in comparison with that of amorphous phases. The nanophase composites are stable in the experimentally measured temperature ranges of 12–143 K with upper temperature limits of 520–619 K (substage 2.4) where crystallization of the intermetallic phases occurs. The analytical model assuming retardation of the diffusion-limited growth due to impingement of the diffusion fields has been applied for description the experimental data and the effective diffusion coefficients governing the growth of nanocrystals in amorphous Al_{86}Ni_{6}Co_{2}Gd_{6} and Al_{90}Y_{10} alloys have been estimated (substage 2.5). There was no scheduling variance in the reporting period.

2. Introduction

Technical progress requires strong and light materials. Al-based amorphous alloys, containing 8–20 at.% rare earths (RE) and transition metals (TM) possess high tensile strength [1,2] as well as high specific strength due to low density of Al and hence attracted increasing interest for a large number of technical applications as light and high-strength structural materials, for example for aerospace applications and so on. Moreover, it has been shown [2-4] that the mechanical properties of amorphous alloys can be essentially improved (about 1.5 times) by partial crystallization, which results in formation of Al particle diameters in the range 3-50 nm, particle separation 10-100 nm, and the α-Al volume fraction 10-30%. However, until now, these properties were obtained in thin ribbons produced by the melt-spinning technique so the application of such nanophase composites as structural materials is restricted. To obtain bulk Al-based materials with nanocomposite
structure, two basic strategies may be used – search the alloy compositions with high glass forming ability [5] and consolidation of melt-spun ribbons or powders with amorphous structure [6,7].

Since the key process which determines the nanocrystal size and their volume density as well the thermomechanical regimes of consolidation required to keep nanocomposite structure is nanocrystallization, the studies of this project stage have been focused on establishment of the mechanisms this process. The activity includes the experimental investigations of thermal stability of amorphous phases in a number of Al-(Ni,Co,Fe)-(Y,Gd) melt-spun ribbons, the estimations of the structural parameters of nanophase composites, the establishment of nanocrystallization mechanisms and the development of the relevant theoretical models of the process of formation nanophase composites.

The main goals of these studies are to obtain information concerning the effect of alloying on thermal stability of amorphous alloys and nanophase composites, on crystallization mechanisms and on the structural parameters of partially crystallized alloys as well as to develop the technique for estimation of the main factors responsible for nanoscale microstructure formation. The obtained results have to provide basis for selection of the alloys with improved both thermal stability and microhardness for subsequent advanced investigations and optimization of their mechanical properties.

3. Methods, Assumptions, and Procedures

In order to estimate of the influence of alloying on glass forming ability of Al-based melts as well as on thermal stability, structure, microhardness, mechanisms of nanocrystallization of amorphous phases a series of 12 binary, ternary, quaternary and quinary Al_{90-86}(Ni,Co,Fe)_{6-8}(Y,Gd,Tb)_{6-10} alloys has been prepared by arc melting under highly purified argon atmosphere and rapidly quenched from liquid state by the melt-spinning processing under a helium atmosphere.

Glass forming ability of the alloys has been qualitative estimated at this stage from the specific features of the X-ray diffraction patterns. Thermal stability of both amorphous phases and partially crystallized nanocomposite structures has been studied by monitoring of electrical resistance changes under continuous constant rate heating.

The structural parameters of nanophase composites (average size of nanocrystals, their volume density and the volume fraction) have been estimated from X-ray diffraction data. For estimation of crystallization mechanisms the isothermal kinetic crystallization curves obtained by combination of electrical resistance measurements and X-ray analysis data have been used.

The relatively simple analytical model, describing changes of sizes of Al nanocrystals versus time at constant temperature, has been proposed and the values of the effective diffusion coefficient, which governs the growth of nanocrystals, have been estimated from comparison between the calculated and experimental data.

The effect of nanocrystallization on mechanical properties has been estimated from the microhardness measurements.

Amorphous Al_{90.86}(Ni,Co,Fe)_{6.8}(Y,Gd,Tb)_{6.10} alloys have been obtained by single roller melt spinning technique in the form of ribbons 5–10 mm wide and 35–90 μm thick as described in the previous annual report.

The electrical resistance of ribbons has been measured in situ by the automated four-probe dc method in which thermal emf effects were accounted by averaging for positive and negative voltages. Electrical contacts to the samples of as-cast and heat-treated ribbons were made by spot-welding of silver wires about 50 μm in diameter.

The constant heating experiments were performed at scan rates ranging from 5 to 40 K/min using a standard PRT-1000 device. The measurements of the electrical resistance at continuous heating has shown that it drops at several (from 2 to 2) stages as illustrated in Fig.1 for amorphous Al_{90}Y_{10} alloy. The X-ray diffraction patterns of the samples heated to the temperatures above each stage which are clearly resolved in dR/dT curves has shown that each stage results in structural changes (Fig. 2). It indicates that crystallization of the amorphous Al_{90}Y_{10} alloy is multi-stage process which is typical for Al-based glasses [8,9]. It should be noted that as it has been shown in [8] the resistometry scan of the Al_{85}Ni_{5}Y_{8}Co_{2} glass not only well agrees with the DSC thermogram, but is more sensitive for the detection of the phase transformations. Therefore, the characteristic temperatures of amorphous → crystalline transformation (onset crystallization, $T_{on}$, and maximum rate of crystallization, $T_{X}$) in the present study have been determined from the resistometric data as shown in Fig. 1.
Fig. 1. Changes of normalized resistance (left axis) and the derivative of $\frac{dR}{dT}$ (right axis) during heating of amorphous Al$_{90}$Y$_{10}$ melt spun ribbon recorded at heating rate of 5 K/min, where $R_0$ is the electrical resistance at room temperature. The arrow shows the onset crystallization temperature.

Isothermal anneals were carried out by immersing small pieces of melt-spun ribbons in silicone oil (below 573 K) or salt (eutectic mixture of NaNO$_3$, KNO$_3$ and LiNO$_3$) baths with temperature controlled to ± 1.0 K. The measured heat-up times in the liquid baths were typically from 3 to 4 s.

The structural characterization of the partially crystallized ribbons was carried out by X-ray diffraction using Fe-filtered CoKα radiation ($\lambda = 0.1791$ nm) in a standard DRON-3M diffractometer. The amorphous and nanocrystalline total intensity contributions, shown in Fig. 2 (a) were obtained by deconvolution [10] of the first amorphous halo and the two most intense ((111) and (200)) fcc-Al peaks after background subtraction. The Lorentzian function fits were chosen for matching both amorphous halo and broadened fcc-Al peaks according to the best agreement with experimental data.

The special attention in this part of studies was paid to determination of the volume fraction of Al nanocrystals, $X$, in the partially crystallized samples with nanocomposite structure, because there is no well established technique of evaluation of this quantity. The comparative analysis presented in Ref. [11] has shown that the widely used relation [12]

$$X = A_c / (A_a + A_c)$$

(1)

(where $A_c$ and $A_a$ being the sum of the areas of the (111) and (200) reflections of Al and that of amorphous halo, respectively) underestimates the volume fraction of Al nanocrystals in a residual amorphous matrix. The physical reason of this is an enhanced average scattering power of the amorphous phase in comparison with that of pure Al. It has been proposed to use multiplying the value of $A_a$ by a correction factor (less than unity) [13] or the Rietveld procedure [11] to account the discrepancy in estimations of $X$. The more direct approach to account the difference between the scattering power of amorphous and nanocrystalline phases of different chemical compositions was proposed in Ref. [14]

$$\frac{A_c}{A_c + A_a} = \frac{X(f)}{X(f)^2 + (1 - X(f))},$$

(2)

where $<f>$ is the average scattering factors of amorphous matrix and nanocrystalline phase. The above mentioned approaches for estimation of $X$ were used to determine the volume fraction of Al nanocrystals in the samples of the binary amorphous Al$_{90}$Y$_{10}$ alloy heated up to the temperatures corresponding the end of the first and second crystallization stages (Fig. 1).

The values of $X$ in the sample after the first crystallization stage calculated from Equations (1) and (2) were 29 and 45%, respectively. In view, that the dominating process of the second crystallization stage is formation of the Al$_3$Y intermetallic compound which volume fraction in the fully crystallized sample according the level rule is 40 %, the volume fraction of Al nanocrystals after nanocrystallization calculated from Eq. (2) seems rather reasonable. It should be also noted that the calculated difference between $X$ calculated from Eq. (1) and...
(2) is close to that obtained from Eq. (1) and from Rietveld method for $\text{Al}_{87}\text{Ni}_{7}\text{La}_{5}\text{Zr}_{1}$ \cite{11} and corresponds the value of 0.5 for the correction factor proposed in Ref. \cite{13}.

The microhardness ($H\mu$) measurements of the heat treated melt-spun ribbons were performed using standard PMT-3 microhardness tester calibrated with a NaCl monocrystal. The measurements were carried out on the flat areas presumably contact surfaces of 15 specimens at a load of 0.29 N (30 gf) during 10 s. The $H\mu$ values for each specimen were determined by averaging of 10 indents with regular shape which gave the standard deviation of the data about ±1.5%.

4. Results and Discussion

Activity 2. Clarification of regularities of the Al-nanocomposite formation processes

As it has been mentioned above, the nanocomposite structures formed in partially crystallized Al-based alloys are the most important from practical point of view. Therefore, at this project stage the nanocrystallization process is the main focus of the studies aimed to clarify it. These studies include the experimental determination of thermal stability of both amorphous and partially crystallized structures, estimation of the structural parameters of nanophase composites, kinetics and mechanisms of nanocrystallization and development of relevant theoretical models describing formation of nanocrystals in amorphous phases. The results of these studies will provide the basis for quantitative analysis of the process of formation nanophase composites.

Activity 2.1. Studies of thermal stability of the amorphous phases and crystallization behaviour during heat treatment of the Al-based alloys with various chemical composition

Thermal stability of amorphous state is a very important property of amorphous alloys which marks limiting temperatures (at continuous heating) or times (at isothermal conditions) of their existence. In the present study the crystallization onset temperature, $T_{\text{ons}}$, determined at heating rate of 5 K/min (Fig. 1) has been taken as a measure of kinetic thermal stability of glassy alloys with various chemical composition. For this purpose the measurements of the electrical resistance of the melt-spun ribbons have been carried out and the obtained curves are shown in Fig. 3.

As can be seen in this Figure both the thermal stability and crystallization behavior of the amorphous Al-based alloys depend on their chemical composition, however, the alloying effects are ambiguous. In fact, the full and even partial replacement of Y by Gd in $\text{Al}_{87}\text{Ni}_{7}\text{Gd}_{5}$ alloy results in essential lowering of thermal stability (Fig 3a,b), in contrast to higher $T_{\text{ons}}$ of binary $\text{Al}_{90}\text{Gd}_{10}$ alloy in comparison with that of $\text{Al}_{90}\text{Y}_{10}$ (Fig. 3a). At the same time the variations of content of transition metals have an evident effect on thermal stability of amorphous phases, namely partial substitution of Ni for Co and especially Fe increases $T_{\text{ons}}$ (Fig. 3b,c).

Note, that the positive effect of Ni replacement with Co or especially Fe increases $T_{\text{ons}}$ (Fig. 3b,c). Note, that the positive effect of Ni replacement with Co or Fe on thermal stability amorphous Al-(Ni,Co,Fe)-RE alloys has been recently reported in literature \cite{15-17}. Besides, the change of Ni/(Co,Fe) proportions from 3/1 to 1/3 leads to lowering of the number of crystallization stages from 3 (which is typical for the majority amorphous alloys studied) to 2 (Fig. 3c).

The values of the onset crystallization temperatures summarized in Table 1 range from 440 K ($\text{Al}_{90}\text{Ni}_{7}\text{Fe}_{4}\text{Gd}_{5}$) to 584 K ($\text{Al}_{90}\text{Ni}_{7}\text{Fe}_{6}\text{Gd}_{6}$) and are rather high in comparison with those reported in literature for Al-based amorphous alloys (e.g., \cite{15-18}).

The continuous heating experiments at rates of 5, 10, 20 and 40 K/min were used to determine the activation energy of the first crystallization stage, $Q_1$, which is a useful parameter of the crystallization process. For this purpose the well-known method proposed by Kissinger \cite{19} was used. In the standard Kissinger analysis of a nucleation-and-growth process the activation energy is determined by plotting, for a number of scans at different rates, $q$, $\ln(T_X/q)$ vs. $(1/T_X)$, where $T_X$ is the peak temperature (maximum rate) of transformation determined as shown in Fig. 1. The slope of a straight line fit through the plot is then $Q/k_B$ ($k_B$ being the Boltzmann constant).

The results of these experiments presented in Fig. 4 show that the crystallization temperatures $T_{X1}$ in the Kissinger coordinates are close to the straight lines which indicates the correctness of the analysis. Such determined activation energies of the first crystallization stage of the amorphous alloys investigate are in the wide range from 17000 to 65800 K (1.47 – 5.7 eV) (Table 2). All these values agree with those estimated for
Table 1. Chemical composition, average ribbon thickness, number of crystallization stages and thermal stability of the amorphous alloys

<table>
<thead>
<tr>
<th>Alloy composition</th>
<th>No of casting run</th>
<th>Thickness, μm</th>
<th>Number of stages</th>
<th>$T_{onset}$, K</th>
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<tbody>
<tr>
<td>1. Al$<em>{86}$Y$</em>{10}$</td>
<td>B-275</td>
<td>38 ± 6</td>
<td>2</td>
<td>464 ± 1</td>
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<tr>
<td>2. Al$<em>{86}$Gd$</em>{10}$</td>
<td>B-272</td>
<td>27 ± 2</td>
<td>3</td>
<td>476 ± 1</td>
</tr>
<tr>
<td>3. Al$<em>{86}$Ni$</em>{8}$Y$_{5}$</td>
<td>B-112</td>
<td>52 ± 5</td>
<td>3</td>
<td>484 ± 1</td>
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<td>4. Al$<em>{86}$Ni$</em>{8}$Gd$_{5}$</td>
<td>B-252</td>
<td>35 ± 3</td>
<td>3</td>
<td>453 ± 1</td>
</tr>
<tr>
<td>5. Al$<em>{86}$Ni$</em>{8}$Gd$<em>{1}$Y$</em>{4}$</td>
<td>B-254</td>
<td>45 ± 5</td>
<td>3</td>
<td>440 ± 1</td>
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<tr>
<td>6. Al$<em>{86}$Ni$</em>{8}$Co$<em>{2}$Gd$</em>{6}$</td>
<td>B-276</td>
<td>50 ± 10</td>
<td>3</td>
<td>501 ± 1</td>
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<tr>
<td>7. Al$<em>{86}$Ni$</em>{8}$Co$<em>{2}$Gd$</em>{6}$</td>
<td>B-277</td>
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<td>2</td>
<td>545 ± 1</td>
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<td>8. Al$<em>{86}$Ni$</em>{8}$Co$<em>{2}$Gd$</em>{1}$Y$<em>{2}$Tb$</em>{1}$</td>
<td>B-173</td>
<td>48 ± 10</td>
<td>3</td>
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<tr>
<td>9. Al$<em>{86}$Ni$</em>{8}$Fe$<em>{2}$Gd$</em>{6}$</td>
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<td>10. Al$<em>{86}$Ni$</em>{8}$Fe$<em>{2}$Gd$</em>{1}$Y$_{4}$</td>
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<td>509 ± 1</td>
</tr>
<tr>
<td>12. Al$<em>{86}$Ni$</em>{8}$Fe$<em>{2}$Gd$</em>{6}$</td>
<td>B-289</td>
<td>41 ± 3</td>
<td>2</td>
<td>584 ± 1</td>
</tr>
</tbody>
</table>
Al-based amorphous alloys (e.g. [15-18]) and are higher (except Al$_{90}$Gd$_{10}$) than $Q$ of self-diffusion in pure Al (17130 K) [19] which indicates that the first crystallization stage of Al-based amorphous alloys is governed by diffusion of the solute atoms (transition and rare earth metals). In view, that due to technological difficulties the structure of the Al$_{90}$Gd$_{10}$ as prepared melt-spun ribbon was partially crystallized (Rep Qtrl_5) the value of $Q_1$ for this alloy may be underestimated. For this reason this amorphous alloy has been excluded from subsequent analysis. It should be noted that in contrast to the data of Ref. [15-17], there are no direct correlation between thermal stability of the amorphous phases and the activation energies of the first crystallization stage (Table 2). The possible reason for this is differences in the mechanisms of the first crystallization stage in Al-based amorphous alloys with different chemical compositions and this problem has been considered below.

In order to clarify the nature the processes which occur during transition of amorphous phases into crystalline state the X-ray diffraction studies of the samples heated up to the end temperatures of each crystallization stage have been performed. The analysis of the X-ray diffraction patterns has shown that crystallization of the majority of the ternary and quaternary amorphous alloys investigated crystallize in three stage with Al nanocrystals formation in the first stage (Fig. 5a,b). However, the character of the phases formed in the second and third stages are different and less clear. As it can be seen in Fig. 5a after the second crystallization stage structure of partially crystallized Al$_{86}$Ni$_6$Co$_2$Gd$_6$ alloy remains essentially unchanged, i.e. no additional phases form. The similar behavior has been observed during crystallization of amorphous Al$_{85}$Ni$_7$Gd$_8$ alloy [22] and has been interpreted as local chemical ordering which occurs in the residual amorphous matrix. Though the detailed analysis of the X-ray diffraction patterns has shown that the relative intensity of the fcc Al (111) and (200) reflections increases whereas their breadth decreases which indicates that growth of Al nanocrystals occurs at this crystallization stage. Heating to the end of the third stage induces of formation of one or more
intermetallics (Fig. 5a) which structure has not yet been identified in the present study. The similar phase formation sequence has been also observed during crystallization of amorphous Al_{86}Ni_{6}Co_{2}Gd_{6}Y_{2}Tb_{1} and Al_{86}Ni_{6}Fe_{2}Gd_{6} alloys.

Table 2. Chemical composition, structure of the alloys after the first crystallization stage and activation energies.

<table>
<thead>
<tr>
<th>Alloy composition</th>
<th>No of casting run</th>
<th>Type of NC structure</th>
<th>$Q_{1}$, K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al$<em>{90}$Y$</em>{10}$</td>
<td>B-275</td>
<td>Al</td>
<td>22600 ± 200</td>
</tr>
<tr>
<td>Al$<em>{90}$Gd$</em>{10}$</td>
<td>B-272</td>
<td>Al</td>
<td>17000 ± 1600</td>
</tr>
<tr>
<td>Al$<em>{87}$Ni$</em>{8}$Y$_{5}$</td>
<td>B-112</td>
<td>Al</td>
<td>22700 ± 900</td>
</tr>
<tr>
<td>Al$<em>{87}$Ni$</em>{8}$Gd$_{5}$</td>
<td>B-252</td>
<td>Al</td>
<td>32100 ± 6200</td>
</tr>
<tr>
<td>Al$<em>{87}$Ni$</em>{8}$Gd$<em>{5}$Y$</em>{4}$</td>
<td>B-254</td>
<td>Al</td>
<td>24800 ± 1600</td>
</tr>
<tr>
<td>Al$<em>{86}$Ni$</em>{8}$Co$<em>{2}$Gd$</em>{6}$</td>
<td>B-276</td>
<td>Al</td>
<td>34300 ± 3500</td>
</tr>
<tr>
<td>Al$<em>{86}$Ni$</em>{8}$Co$<em>{2}$Gd$</em>{6}$Y$_{4}$</td>
<td>B-277</td>
<td>Al + IC</td>
<td>32800 ± 1200</td>
</tr>
<tr>
<td>Al$<em>{87}$Ni$</em>{8}$Fe$<em>{2}$Gd$</em>{6}$</td>
<td>B-251</td>
<td>Al</td>
<td>64700 ± 16200</td>
</tr>
<tr>
<td>Al$<em>{87}$Ni$</em>{8}$Fe$<em>{2}$Gd$</em>{6}$Y$_{4}$</td>
<td>B-257</td>
<td>Al</td>
<td>65800 ± 15600</td>
</tr>
<tr>
<td>Al$<em>{86}$Ni$</em>{8}$Fe$<em>{2}$Gd$</em>{6}$</td>
<td>B-287</td>
<td>Al</td>
<td>31000 ± 1900</td>
</tr>
<tr>
<td>Al$<em>{86}$Ni$</em>{8}$Fe$<em>{2}$Gd$</em>{6}$</td>
<td>B-289</td>
<td>Al+IC</td>
<td>28400 ± 6000</td>
</tr>
</tbody>
</table>

Somewhat different crystallization behavior has been established in a number of another amorphous alloys (Al$_{87}$Ni$_{8}$Gd$_{5}$, Al$_{87}$Ni$_{8}$Y$_{5}$, Al$_{87}$Ni$_{8}$Gd$_{1}$Y$_{4}$, Al$_{87}$Ni$_{4}$Fe$_{2}$Gd$_{5}$ and Al$_{87}$Ni$_{4}$Fe$_{2}$Gd$_{5}$) investigated where the second crystallization stage in amorphous corresponds to the formation of crystals one or several intermetallic phases as illustrated for Al$_{87}$Ni$_{8}$Gd$_{5}$ alloy in Fig. 5b. As can be seen in this Figure the positions of the peaks remain unchanged while they become somewhat narrower, i.e. growth of the phase precipitation is the main event at the third crystallization stage. These observations agree with the results reported in Ref. [23] for amorphous Al$_{87}$Ni$_{8}$Y$_{5}$ alloy where phases formed at the second crystallization stage were identified to be Al$_{1}$Ni and Al$_{23}$Ni$_{6}$Y$_{4}$. However, these data are in disagreement with those of Ref. [17], where for amorphous Al$_{87}$Ni$_{8}$Gd$_{5}$, Al$_{87}$Ni$_{8}$Y$_{5}$, Al$_{87}$Ni$_{8}$Gd$_{1}$Y$_{4}$, Al$_{87}$Ni$_{4}$Fe$_{2}$Gd$_{5}$ and Al$_{87}$Ni$_{4}$Fe$_{2}$Gd$_{5}$ alloys the phase formation sequence shown in Fig. 5a has been reported. One of the possible reasons of this controversy may be using of isothermal annealing in this study which may result in different crystallization path compared with that at constant rate heating [22].

The last two studied amorphous Al$_{86}$Ni$_{6}$Co$_{2}$Gd$_{6}$ and Al$_{86}$Ni$_{6}$Fe$_{2}$Gd$_{6}$ alloys have a two-stage crystallization process (Fig. 5c) in which nanocrystals of Al together with another intermetallic phase(s) nanosized crystals form in the first stage (IC). These unidentified intermetallics are metastable and disappear in the second crystallization stage (Fig. 5c). Note that multi-phase crystallization behavior in the first stage has been observed in a number of the Al-based amorphous alloys (e.g., in Al$_{80}$La$_{2}$Ni$_{5}$ [24] and in Al$_{87}$Ni$_{3}$Co$_{2}$Nd$_{6}$ [16]) and it has been considered as eutectic crystallization. As it has been shown in Ref. [16] the change of the crystallization mode of the first stage is caused by partial replacement of Ni in amorphous Al$_{87}$Ni$_{7}$Nd$_{6}$ by Co. There have been only a few papers in the literature reporting the "eutectic" crystallization mode of Al-based glasses so both the kinetics and mechanism of this process are not established.
Activity 2.2. Experimental studies of kinetics and mechanisms of nanocrystallization of amorphous Al-based alloys

As it has been shown in previous section there are several paths of crystallization process in the amorphous Al-based alloys investigated. In view of the essential improvement of the mechanical properties caused by formation of nanocomposite structures it is quite important to study the mechanisms of nanocrystallization. The most proper way to clarify the mechanism of the crystallization process includes the experimental studies of the process kinetics, structure of crystallized samples and analysis of the results within appropriate theoretical models.

Formation of nanocomposite structures occurs in the first crystallization stage of all amorphous alloys investigated, and in the majority cases they consist of Al nanocrystals embedded in residual amorphous matrix while in some cases (alloys enriched both in Co and Fe) nanoscale intermetallic compounds form simultaneously with Al as illustrated in Figures 6 and 7 respectively.
To clarify the features of kinetics of these two types of nanocrystallization the volume fractions of crystalline phases, \( X \), have been determined from the X-ray diffraction patterns of the samples heated up to temperatures of the end of the first crystallization stage (similar to those shown in Figs. 6 and 7) and the experimentally measured changes of relative electrical resistance \( R(T)/R_0 \) have been converted into the kinetic nanocrystallization curves \( X(T) \). For better visualization the \( X(T) \) curves were numerically differentiated and such obtained dependencies of the nanocrystallization rate on temperature (similar to DSC scans [8]) are shown in Figures 8 and 9.

The common feature of all curves is the tails observed at high temperature sides of the nanocrystallization rate peaks which is typical for the first crystallization stage of amorphous Al-based alloys [25]. However, in the case of multi-phase nanocrystallization the rate of transformation increases by step-wise manner (curves 3 in Figs. 8, 9) while rate of formation of Al nanocrystals increases with temperature gradually. Note that similar changes of the maxima of the heat flow corresponding to the first crystallization stage resulted from partial replacement of Ni with Co have been observed at the DSC thermograms of amorphous Al\(_{87}\)Ni\(_{8-x}\)Co\(_x\)La\(_5\) alloys [15].

Fig. 6. X-ray diffraction patterns of the samples heated up at 5 K/min to temperatures of the first crystallization stage end: 1 – Al\(_{87}\)Ni\(_4\)Fe\(_4\)Gd\(_5\), 2 – Al\(_{87}\)Ni\(_4\)Fe\(_4\)Gd\(_5\)Y\(_4\).

Fig. 7. X-ray diffraction patterns of the samples heated up at 5 K/min to temperatures of the first crystallization stage end: 1 – Al\(_{87}\)Ni\(_4\)Co\(_4\)Gd\(_5\), 2 – Al\(_{87}\)Ni\(_4\)Fe\(_4\)Gd\(_5\).

Fig. 8. Effect of partial replacement of Ni with Co on the rate of the first stage of crystallization of the Al-based amorphous alloys at 5 K/min: 1 – Al\(_{86}\)Ni\(_6\)Co\(_2\)Gd\(_6\); 2 – Al\(_{86}\)Ni\(_6\)Co\(_2\)Gd\(_6\); 3 – Al\(_{86}\)Ni\(_2\)Co\(_6\)Gd\(_6\).

Fig. 9. Effect of partial replacement of Ni with Fe on the rate of the first stage of crystallization of the Al-based amorphous alloys at 5 K/min: 1 – Al\(_{87}\)Ni\(_8\)Gd\(_5\); 2 – Al\(_{87}\)Ni\(_4\)Fe\(_2\)Gd\(_5\); 3 – Al\(_{86}\)Ni\(_2\)Fe\(_4\)Gd\(_6\).
For more detailed analysis of mechanisms of nanocrystallization the studies of isothermal crystallization kinetics at different annealing temperatures have been performed. Several examples of the isothermal kinetic crystallization curves, \( X(t) \), obtained from the measurements of the electrical resistance changes of the amorphous alloys with various nanocrystallization modes are shown in Fig. 10. As it can be seen from this data in the case of nanocrystallization of Al (Fig. 10 a,b) the crystallized volume fraction increases with time with saturation, whereas in the case of multi-phase nanocrystallization (Fig 10c) \( X(t) \) changes sigmoidally. The former behavior of \( X(t) \) is typical not only for nanocrystallization of many amorphous Al-based alloys, but also for the nanocrystal forming Fe-based FINEMET alloys (e.g., [26-28]) and it is assumed to be related with lowering of the rate of crystal growth. On the contrary, the sigmoidal shape of the kinetic curve of multi-phase nanocrystallization is typical for the majority of the metallic glasses [29] crystallizing into structures with relatively coarse grain size.

The experimentally measured kinetic crystallization curves \( X(t) \) have been used to obtain information the possible nanocrystallization mechanisms within the commonly used for this purpose classical Kolmogorov-Johnson-Mehl-Avrami (KJMA) theory [30]. This theory describes the transformed under isothermal conditions volume fraction on time as \( X(t) = 1 - \exp (-Kt^n) \) with \( K \) being the kinetic constant. The so-called Avrami exponent, \( n \), characterizes the dimensionality of the transformation and depends on whether the transformation is interface or diffusion controlled and on the nucleation rate. In order to estimate the values of \( n \) the kinetics crystallization curves shown in Fig. 10 have been plotted as \( \ln(-\ln(1 - X)) \) versus \( \ln(t) \).

The common feature of the plots presented in Figures 11–13 for the alloys investigated (as well as for the amorphous nanocrystals forming Al- and Fe-based alloys [27,28]) is considerable deviation from straight lines.
pointing to the failure of the KJMA equation or at least to it applicability only to the initial stage of nanocrystallization. The theoretical analysis of the nanocrystallization process has shown that the gradual lowering of the Avrami exponent in the course of transformation may be caused with blocking of the nanocrystals growth [27,28], which is not accounted the KJMA model. Nevertheless, the data presented in Figures 11–13 allow making several assumptions about mechanisms of nanocrystallization in the amorphous Al-based alloys investigated.

As shown in Fig. 11, the slopes of the straight lines provide an Avrami exponent of 1 for initial stages of Al-nanocrystals formation in amorphous Al90Y10 alloy at different annealing temperatures. In the light of generally accepted interpretation [30] this value of n corresponds to two-dimensional diffusion controlled growth. Note, that similar value of n has been found for amorphous Al88La2Gd6Ni4 in which three-dimensional diffusion-controlled growth of Al nanocrystals has been established by microstructural analysis [27]. In view, that value of \( n = 1 \) for Al90Y10 alloy has been found for different annealing temperatures (Fig. 11) this result allows suggestion that nanocrystallization of this amorphous alloy occurs by diffusion-controlled growth of the pre-existing (the most probably quenched-in) Al nuclei the high density of which retards the grain growth during the crystallization process.

In contrast to Al90Y10 alloy the value of Avrami exponent at initial stages of nanocrystallization of amorphous Al86Ni6Co2Gd6 alloy is strongly dependent on annealing temperature and is found to be 2.6 and 0.26 at 461 and 501 K, respectively (Fig. 12). The former value of \( n \) is close to 2.5 which indicates diffusion-limited growth with steady-state nucleation [30]. Note, that this crystallization mechanism has been identified experimentally in amorphous Al85Ni5Y8Co2 alloy [8] where, in part, has been established that nucleation of Al nanocrystals takes place only at initial stage of the process. It assumes that lowering \( n \) with temperature in this alloy may be caused by retardation of both the nucleation and growth processes. While retardation of growth may be result from impingement of the diffusion fields, the blocking of nucleation may be caused by the increase of the total concentration of alloying elements in the residual amorphous matrix which hinders the formation of pure Al nuclei. To validate the suggested nanocrystallization mechanism of amorphous Al86Ni6Co2Gd6 alloy it is necessary to estimate the parameters of nanocomposite structures obtained at different temperatures and this results will be presented in the next section.

![Avrami plots for amorphous Al90Y10 alloy from the data presented in Fig. 10(a) for annealing temperatures 447 K (a) and 460 K (b).](image-url)
increase of the total concentration of alloying elements in the residual amorphous matrix which hinders the formation of pure Al nuclei. To validate the suggested nanocrystallization mechanism of amorphous Al_{86}Ni_{6}Co_{2}Gd_{6} alloy it is necessary to estimate the parameters of nanocomposite structures obtained at different temperatures and this results will be presented in the next section.

Fig. 12. Avrami plots for amorphous Al_{86}Ni_{6}Co_{2}Gd_{6} alloy from the data presented in Fig. 6 (b) for annealing temperatures 461 K (a) and 501 K (b).

The appreciably higher values of the Avrami exponents have been found for the initial stages of nanocrystallization of amorphous Al_{86}Ni_{6}Co_{2}Gd_{6} alloy where intermetallic compound(s) crystallizes simultaneously with Al (Fig. 13). As can be seen the value of $n$ has a tendency to lowering with annealing temperature from 5.6 to 4. The latter value of $n$ corresponds the case of interface controlled crystallization with constant rates of crystal nucleation and three-dimensional growth, while $n > 4$ indicates of transient nucleation with increasing frequency [30]. At first sight, these estimations are in agreement with supposed above eutectic crystallization mechanism for amorphous Al_{86}Ni_{6}Co_{2}Gd_{6} and Al_{86}Ni_{2}Fe_{6}Gd_{6} alloys similar to that identified for alloy Al_{89}La_{6}Ni_{5} [24]. However, both lowering of $n$ in the course of multi-phase crystallization and lack in the literature of microstructural studies of the partially crystallized samples leave the proposed eutectic mechanism of this process not clear identified.

Fig. 13. Avrami plots for amorphous Al_{86}Ni_{6}Co_{2}Gd_{6} alloy from the data presented in Fig. 6 (c) for annealing temperatures 525 K (a) and 560 K (b).

To summarize this section it can be said that analysis of nanocrystallization kinetics of the amorphous alloys reveals several underlying mechanisms: (i) diffusion-controlled growth of the pre-existing Al nuclei (Al_{89}Y_{10}), (ii) nucleation and diffusion-limited growth of Al nanocrystals (Al_{86}Ni_{6}Co_{2}Gd_{6}), and (iii) eutectic-like transformation by transient nucleation and interface controlled growth of nanocrystals of Al and intermetallic
compound(s) (Al$\text{$_86$}Ni$\text{$_2$}Co$\text{$_6$}Gd$\text{$_6$}$). Further work is required to understand the origin of lowering of Avrami exponent in the course of nanocrystallization as well as to establish the possible mechanisms of nucleation.

Activity 2.3 Determination of the parameters of nanocomposite structures as a function of alloy chemical composition and thermal prehistory of the amorphous Al-based alloys

As it has been shown above (Figs. 5–7) a general microstructural feature of the investigated amorphous Al-TM-RE alloys after the first crystallization stage is presence of nanoscale crystals of Al (in some cases with intermetallics) in a residual amorphous matrix. As it is known from the literature [2–4, 26, 31–33] formation of such nanocomposite structures leads to essential strengthening of Al-based alloys which is of practical importance. Despite the strengthening mechanisms in such nanocomposite structures are controversial [4, 26, 32], it is established that mechanical properties are strongly dependent on the crystallized volume fraction while the effects of the size and volume density of Al nanocrystals have not been studied. In order to elucidate these effects the influence of the chemical composition and the heat treatment regimes on the size and volume density of Al nanocrystals have been studied.

The volume fraction of nanocrystalline Al has been estimated in the samples heated up the end of the first crystallization stage from the X-ray diffraction patterns similar to those shown in Figs. 6 and 7 using Eq. 2. Size of Al nanocrystals have been calculated from the Sherrer formula

\[ L = \frac{0.9 \lambda}{B \cos \theta_B} \]

where \( B \) is the breadth (full width at half-maximum) of the (111) peak and \( \theta_B \) is the angular position of the center of the peak. In turn, using the values of these parameters the volume densities of Al nanocrystals have calculated as

\[ N = \frac{6X}{\pi L^3} \]

Such estimated values of the structural parameters of nanocomposites are listed in Table 3. Note, that in the case of formation more that one nanocrystalline phase the total volume of the crystalline phases has been calculated from Equation (1). These compositions are marked by * in Table 3.

As it can be seen, the crystallized volume fractions, the average sizes of Al nanocrystals and their densities formed in the first crystallization event are in the ranges (0.22–0.59), (14.8–21.0) nm and (1.1–4.3) \( \times 10^{23} \) m\(^{-3}\), respectively. The lattice parameters of fcc Al nanocrystals have been found to be about 0.450 nm in all samples with nanocomposite structure which coincides with that of pure Al. These values are in general agreement with those found in other Al-based alloys with nanocomposite structure (e.g., [8, 26, 34]). We have note here that any systematic correlation between the chemical composition of the amorphous alloys and the nanophase composite parameters is not evident.

Table 3. Chemical composition, structural parameters of nanophase composites, their microhardness and its increment after the first crystallization stage of continuously heated samples.

<table>
<thead>
<tr>
<th>Alloy composition</th>
<th>No of casting run</th>
<th>( L ), nm</th>
<th>( X )</th>
<th>( N ), m(^{-3})</th>
<th>( H ) after 1 stage, MPa</th>
<th>( \Delta H ), MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al$<em>{90}$Y$</em>{10}$</td>
<td>B-275</td>
<td>15.7</td>
<td>0.4</td>
<td>2( \times 10^{23} )</td>
<td>3950</td>
<td>1700</td>
</tr>
<tr>
<td>Al$<em>{87}$Ni$</em>{8}$Y$_{5}$</td>
<td>B-112</td>
<td>20.1</td>
<td>0.59</td>
<td>1.4( \times 10^{24} )</td>
<td>5200</td>
<td>1720</td>
</tr>
<tr>
<td>Al$<em>{87}$Ni$</em>{8}$Gd$_{5}$</td>
<td>B-252</td>
<td>15.6</td>
<td>0.38</td>
<td>3.5( \times 10^{23} )</td>
<td>5180</td>
<td>2130</td>
</tr>
<tr>
<td>Al$<em>{87}$Ni$</em>{8}$Gd$<em>{5}$Y$</em>{4}$</td>
<td>B-254</td>
<td>14.8</td>
<td>0.32</td>
<td>3.5( \times 10^{23} )</td>
<td>4880</td>
<td>1740</td>
</tr>
<tr>
<td>Al$<em>{88}$Ni$</em>{9}$Co$<em>{5}$Gd$</em>{6}$</td>
<td>B-276</td>
<td>15.6</td>
<td>0.44</td>
<td>2.2( \times 10^{23} )</td>
<td>4360</td>
<td>1000</td>
</tr>
<tr>
<td>Al$<em>{88}$Ni$</em>{9}$Co$<em>{5}$Gd$</em>{6}$*</td>
<td>B-277</td>
<td>15.4</td>
<td>0.22</td>
<td>1.1( \times 10^{23} )</td>
<td>5100</td>
<td>1630</td>
</tr>
<tr>
<td>Al$<em>{87}$Ni$</em>{9}$Fe$<em>{4}$Gd$</em>{5}$</td>
<td>B-251</td>
<td>18.7</td>
<td>0.41</td>
<td>2.2( \times 10^{23} )</td>
<td>4890</td>
<td>1430</td>
</tr>
<tr>
<td>Al$<em>{87}$Ni$</em>{9}$Fe$<em>{4}$Gd$</em>{5}$Y$_{4}$</td>
<td>B-257</td>
<td>16.4</td>
<td>0.51</td>
<td>4.3( \times 10^{23} )</td>
<td>4830</td>
<td>1400</td>
</tr>
<tr>
<td>Al$<em>{86}$Ni$</em>{9}$Fe$<em>{6}$Gd$</em>{6}$</td>
<td>B-287</td>
<td>20.6</td>
<td>0.25</td>
<td>1.1( \times 10^{23} )</td>
<td>4120</td>
<td>740</td>
</tr>
<tr>
<td>Al$<em>{86}$Ni$</em>{9}$Fe$<em>{6}$Gd$</em>{6}$*</td>
<td>B-289</td>
<td>16.3</td>
<td>0.31</td>
<td>2( \times 10^{23} )</td>
<td>4940</td>
<td>1380</td>
</tr>
</tbody>
</table>

*) Multiphase structure

In order to study the effect of the heat treatment regime on the parameters of nanophase composites amorphous Al$_{90}$Y$_{10}$, Al$_{87}$Ni$_{9}$Fe$_{4}$Gd$_{5}$ and Al$_{88}$Ni$_{9}$Co$_{5}$Gd$_{6}$ ribbons has been isothermally annealed to the end of the first crystallization stage (for 1800 s at 460 K, for 18000 s at 557 K and for 79200 s at 433 K, respectively). The results of the calculations are listed in Table 4. It is evident that structural parameters of nanophase composites in Al$_{90}$Y$_{10}$ and Al$_{87}$Ni$_{9}$Fe$_{4}$Gd$_{5}$ alloys are practically independent on thermal regime of heat treatment whereas long term annealing of amorphous Al$_{86}$Ni$_{9}$Co$_{5}$Gd$_{6}$ alloy leads to formation of essentially smaller nanocrystals with higher volume density in comparison with those formed at constant rate.
heating. These results suggest that the nucleation process plays an important role in the primary crystallization of Al$_{86}$Ni$_6$Co$_2$Gd$_6$ alloy in contrast to the Al$_{90}$Y$_{10}$ and Al$_{87}$Ni$_4$Fe$_4$Gd$_5$ alloys which crystallize presumably by the diffusion limited growth of the "quenched-in" nuclei.

Table 4. Comparison of the parameters of nanocomposite structures obtained at isothermal conditions and at continuous heating

<table>
<thead>
<tr>
<th>Alloy composition</th>
<th>No of casting run</th>
<th>$X_{1\text{(iso)}}$</th>
<th>$X_{1\text{(heat)}}$</th>
<th>$L_{\text{iso}}$, nm</th>
<th>$L_{\text{heat}}$, nm</th>
<th>$N_{\text{iso}}$, m$^{-3}$</th>
<th>$N_{\text{heat}}$, m$^{-3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al$<em>{90}$Y$</em>{10}$</td>
<td>B-275</td>
<td>0.45</td>
<td>0.4</td>
<td>17.3</td>
<td>17.9</td>
<td>1.7$\times$10$^{23}$</td>
<td>1.3$\times$10$^{23}$</td>
</tr>
<tr>
<td>Al$_{87}$Ni$_4$Fe$_4$Gd$_5$</td>
<td>B-251</td>
<td>0.33</td>
<td>0.41</td>
<td>15.6</td>
<td>18.7</td>
<td>3.1$\times$10$^{23}$</td>
<td>2.2$\times$10$^{23}$</td>
</tr>
<tr>
<td>Al$_{86}$Ni$_6$Co$_2$Gd$_6$</td>
<td>B-276</td>
<td>0.58</td>
<td>0.44</td>
<td>8.5</td>
<td>15.6</td>
<td>1.8$\times$10$^{24}$</td>
<td>2.2$\times$10$^{23}$</td>
</tr>
</tbody>
</table>

It should be noted that the results presented in this section are preliminary and to make the reliable conclusion the systematic studies of the influence of both temperature of isothermal annealing and rate of heating on the parameters of nanocomposite structures will be carried out.

Besides, it was of interest to examine the effect of nanocrystallization on the microhardness of the partially crystallized amorphous alloys. From the results presented in Fig. 14 for two binary alloys it is seen that formation of Al nanocrystals results in essential enhancement of microhardness while crystallization of intermetallic phases leads to lowering of $H_\mu$ which is typical for amorphous Al-TM-RE alloys [3, 4, 33]. The maximum values of $H_\mu$ which reached at the end of the first crystallization stage of the alloys investigated at constant rate heating are listed in Table 3 together with the microhardness increments caused by nanocrystallization. The highest values of $H_\mu$ (about 5200 MPa) and very high its increments (> 1700 MPa) were found in the ternary Al$_{88}$Ni$_8$Y$_8$ and Al$_{89}$Ni$_6$La$_6$ alloys with nanocomposite structures. It is somewhat surprising that both $H_\mu$ and $\Delta H_\mu$ in multiphase nanocomposite structures containing intermetallics in Al$_{86}$Ni$_2$Co$_6$Gd$_6$ and Al$_{88}$Ni$_2$Fe$_6$Gd$_6$ alloys do not exceed those in the partially crystallized alloys containing only Al nanocrystals. It is not yet possible, however, to establish clear correlations between the hardness of nanophase composites obtained at continuous heating and both their structural parameters and chemical compositions except a tendency for $H_\mu$ to increase with increasing of the density Al nanocrystals and due to partial replacement of Ni with Co or Fe. The $H_\mu$ values of nanophase composite structures formed in Al$_{87}$Ni$_4$Y$_5$, Al$_{87}$Ni$_4$Gd$_5$ and Al$_{88}$Ni$_2$Co$_6$Gd$_6$ alloys (Table 3) are close to the highest values of that found for Al$_{88}$Ni$_4$Y$_8$ (~ 530 kgc/mm$^2$) [26] and Al$_{89}$Ni$_6$La$_6$ (about 540 kgc/mm$^2$) [35].

![Fig. 14. Effect of crystallization on microhardness (right axis) of amorphous Al$_{90}$Y$_{10}$ (a) and Al$_{90}$Gd$_{10}$ (b) alloys.](image)

The detailed investigations of correlations between the mechanical properties of nanocomposite structures and their structural parameters will be performed at the final stage of the project.
Activity 2.4. Studies of the temperature/time limits of stability of nanocomposite structure in the Al-based alloys

It follows from the above (Table 3) that the partially crystallized Al-based alloys with nanocomposite structure which formed at the first crystallization stage have the most attractive potential for structural applications. However, the nanocomposite structure is thermodynamically metastable and subsequent crystallization which takes place at higher temperatures at continuous heating results in the pronounced lowering of the hardness (Fig. 14). It indicates that the studies of kinetics and mechanism of the second crystallization stage are very important for development of high-strength Al-based alloys for elevated temperature applications as well as for estimation of the temperature ranges of consolidation processing of rapidly quenched materials. However, until now the second crystallization stage in Al-based amorphous alloys has been not studied at the proper level (e.g., [35,36]).

As in the case of amorphous phases thermal stability of nanophase composites in the present study has been characterized by the onset crystallization temperature of the second crystallization stage, \( T_{\text{ons2}} \), measured at constant rate heating which has been estimated from the curves \( R(T)/R_0 \) similar to that as \( T_{\text{ons1}} \) (Fig. 1). Such determined values of \( T_{\text{ons2}} \) for the alloys investigated listed in Table 5 are in the relatively wide range of temperatures from 520 K (for Al\(_{90}\)Y\(_{10}\) alloy) to 619 K (for Al\(_{87}\)Ni\(_{8}\)Fe\(_{4}\)Gd\(_{4}\)Y\(_{4}\) alloy). In contrast to the temperatures of first crystallization onset, \( T_{\text{ons1}} \), (Section 2.1) there is no well pronounced correlation between the chemical composition of the alloys and thermal stability of nanocomposite structures.

Table 5. Chemical composition, number of casting run and the parameters of thermal stability of amorphous and nanocomposite alloys

<table>
<thead>
<tr>
<th>Alloy composition</th>
<th>No of casting run</th>
<th>Number of stages</th>
<th>( T_{\text{ons1}}, \text{K} )</th>
<th>( T_{\text{ons2}}, \text{K} )</th>
<th>( \Delta T, \text{K} )</th>
<th>( Q_2, \text{K} )</th>
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<tbody>
<tr>
<td>1 Al(<em>{90})Y(</em>{10})</td>
<td>B-275</td>
<td>2</td>
<td>464 ± 1</td>
<td>520 ± 1</td>
<td>56</td>
<td>22100 ± 1200</td>
</tr>
<tr>
<td>2 Al(<em>{87})Ni(</em>{8})Y(_{4})</td>
<td>B-112</td>
<td>3</td>
<td>484 ± 1</td>
<td>579 ± 1</td>
<td>95</td>
<td>-</td>
</tr>
<tr>
<td>3 Al(<em>{87})Ni(</em>{8})Gd(_{5})</td>
<td>B-252</td>
<td>3</td>
<td>453 ± 1</td>
<td>579 ± 1</td>
<td>126</td>
<td>33000 ± 1200</td>
</tr>
<tr>
<td>4 Al(<em>{87})Ni(</em>{8})Gd(<em>{5})Y(</em>{4})</td>
<td>B-254</td>
<td>3</td>
<td>440 ± 1</td>
<td>583 ± 1</td>
<td>143</td>
<td>30200 ± 3010</td>
</tr>
<tr>
<td>5 Al(<em>{86})Ni(</em>{6})Co(<em>{2})Gd(</em>{6})</td>
<td>B-276</td>
<td>3</td>
<td>501 ± 1</td>
<td>584 ± 1</td>
<td>83</td>
<td>29300 ± 1100</td>
</tr>
<tr>
<td>6 Al(<em>{86})Ni(</em>{6})Co(<em>{2})Gd(</em>{6})</td>
<td>B-277</td>
<td>2</td>
<td>545 ± 1</td>
<td>594 ± 1</td>
<td>49</td>
<td>25000 ± 2000</td>
</tr>
<tr>
<td>7 Al(<em>{87})Ni(</em>{8})Fe(<em>{4})Gd(</em>{5})</td>
<td>B-251</td>
<td>3</td>
<td>506 ± 1</td>
<td>617 ± 1</td>
<td>111</td>
<td>43900 ± 7800</td>
</tr>
<tr>
<td>8 Al(<em>{87})Ni(</em>{8})Fe(<em>{4})Gd(</em>{4})Y(_{4})</td>
<td>B-257</td>
<td>3</td>
<td>497 ± 1</td>
<td>619 ± 1</td>
<td>122</td>
<td>29900 ± 820</td>
</tr>
<tr>
<td>9 Al(<em>{86})Ni(</em>{6})Fe(<em>{2})Gd(</em>{6})</td>
<td>B-287</td>
<td>3</td>
<td>509 ± 1</td>
<td>590 ± 1</td>
<td>81</td>
<td>-</td>
</tr>
<tr>
<td>10 Al(<em>{86})Ni(</em>{6})Fe(<em>{2})Gd(</em>{6})</td>
<td>B-289</td>
<td>2</td>
<td>584 ± 1</td>
<td>596 ± 1</td>
<td>12</td>
<td>11100±1700</td>
</tr>
</tbody>
</table>

Another important parameter of alloys with nanocomposite structure from point of view their subsequent warm consolidation by pressing (e.g., [7]) is difference between the temperatures of the onset of the second and first crystallization stages (\( \Delta T = T_{\text{ons2}} - T_{\text{ons1}} \)). This parameter determines the temperature range in which the consolidation process can be carried out without degradation of the enhanced mechanical properties. As it is evident from Table 5 the largest values of \( \Delta T \) (143, 126 and 122 K) have been found in Al\(_{87}\)Ni\(_{8}\)Gd\(_{4}\)Y\(_{4}\), Al\(_{87}\)Ni\(_{8}\)Gd\(_{6}\) and Al\(_{87}\)Ni\(_{8}\)Fe\(_{4}\)Gd\(_{4}\)Y\(_{4}\) alloys, respectively.

For further characterization of the second crystallization stage the effective activation energy, \( Q_2 \) have been determined using the Kissinger technique [19] as it is shown in Fig. 15. The apparent activation energies of the second crystallization stage are in the range from 11100 to 43900 K (Table 5) and there is no clear correlation between the values of \( Q_2 \) and thermal stability of nanocomposite structures. It is of interest to note that practically all values of \( Q_2 \) which characterizes crystallization of intermetallic compounds are lower than the activation energies of the first crystallization stage (Table 1). It, in particular, may be caused by enrichment of the remaining amorphous matrix by solute atoms such facilitating nucleation of intermetallics. Note, that the reported value of the apparent activation energy of the second crystallization stage 18400 ± 640 K [36] (formation of Al\(_{11}\)(La,Ce)\(_3\) phase) in amorphous Al\(_{87}\)Ni\(_{8}\)Mm\(_3\)Fe\(_{0.5}\) alloy is in the range of \( Q_2 \) values presented in Table 5.
For better understanding of kinetics of the second crystallization stage the samples of two amorphous alloys Al90Y10 and Al86Ni6Co2Gd6 have been annealed at temperatures somewhat lower then T_{onset}2 to observe two crystallization stages in one experiment. As can be seen in Fig. 16 both crystallization stages are clearly revealed by two separate drops in electrical resistance. For estimation of the crystallized volume fractions at each crystallization stage (X1 and X2) the X-ray diffraction patterns of the samples annealed to the end of the first and second crystallization stages (similar to those presented in Figs. 2 and 5) have been used. The values of X1 and X2 determined using Eq. 2 were used for transformation of the R(t) curves to kinetic crystallization curves X(t) shown in Fig. 16 (right axes).

As it is evident from the X-ray diffraction data the sample of Al90Y10 alloy is fully crystallized after second crystallization stage (Fig. 2) while the X-ray diffraction patterns of the Al86Ni6Co2Gd6 sample after first and second crystallization stages are similar (cf. curves 2 and 3 in Fig. 5). As it has been discussed above (Section 2.1) the similar crystallization behavior for amorphous Al85Ni7Gd8 alloy was interpreted as local chemical ordering occurring in the remaining amorphous matrix [22]. However, this explanation seems to be ambiguous accounting the appreciable drop in the resistance and well defined separation between the first and second crystallization stages at continuous heating (Fig. 3c) and isothermal annealing (Fig. 16b). Besides, the value of the average size of the Al nanocrystals after the second crystallization event estimated from the X-ray diffraction pattern presented in Fig. 5a (curve 3) is about 19.6 nm, i.e. 4 nanometers higher than formed at the first crystallization stage (Table 3).

![Fig. 15. Kissinger plots derived from crystallization peak temperatures, T_{X2}, for the amorphous alloys: (a) 1 – Al86Ni2Co6Gd6 (circles), 2 – Al86Ni2CoGd6Y4 (triangles), 3 – Al86NiCo2Gd6 (squares); (b) 1 – Al86Ni2Fe6Gd6 (triangles), 2 – Al87Ni4Fe4Gd5 (squares), 3 – Al87Ni6Gd6 (circles).](image)

![Fig. 16. Changes of the relative electrical resistance (left axis) and the volume fraction transformed (right axis) under isothermal annealing of amorphous alloys (a) Al90Y10 at 487 K and (b) Al86Ni6Co2Gd6 at 575 K.](image)
The isothermal two-stage crystallization curves \( \chi(T) \) of amorphous Al_{86}Ni_{6}Co_{2}Gd_{6} and Al_{80}Y_{10} alloys shown in Fig. 16 were transformed to the Avrami plots (Fig. 17). As can be seen from Fig. 17 the second crystallization stage is also well pronounced in these plots. Besides, these plots at each crystallization stage are not linear which indicates that the processes do not follow the KJMA kinetic equation. Though, from results of linearization of the initial stages of the second crystallization stage (shown by dash lines) some assumptions about transformation mechanisms may be done. In fact, the slope \( n_2 = 2.5 \) for the second (final) stage of crystallization of amorphous Al_{80}Y_{10} corresponds to the process which occurs by steady state nucleation and diffusion-limited growth. This in general agreement with the X-ray diffraction data (Fig. 2, Table 3) which show that in this crystallization stage formation of Al_{3}Y intermetallic compound from the residual amorphous matrix enriched in Y as well coarsening of the Al nanocrystals takes place. In any case both these processes require redistribution of the Al and Y atoms, so the assumed crystallization mechanism seems reasonable.

The Avrami exponent \( n_2 = 1.3 \) established for the second crystallization stage of amorphous Al_{86}Ni_{6}Co_{2}Gd_{6} alloy is comparable and even somewhat higher than that for the first crystallization stage (Fig. 17b) where the diffusion-limited growth of Al nanocrystals is dominating process. Therefore, the similar crystallization mechanism may assumed for the second crystallization stage of Al_{86}Ni_{6}Co_{2}Gd_{6} alloy which, however, needs in subsequent verification.

In conclusion, it should be noted, that the second crystallization stage in the majority of the Al-based alloys investigated begins at temperatures above 573 K (Table 3) which indicates that the materials with nanocomposite structure may be considered as potential candidates for elevated temperature applications.

**Activity 2.5. Development of theoretical models of nanocrystallization at isothermal conditions and upon constant rate heating and comparison with the experimental data**

As it has been established above (Section 2.2) kinetics of formation nanophase composites in amorphous Al-based alloys does not follow the classical KJMA formalism which is widely used for description of glass crystallization including the primary mode [29]. The progressive lowering of the Avrami exponent in the course of nanocrystallization (Figs. 8, 9) which is apparent from the tails observed at high temperature side of the peaks in the \( dX/dT \) vs. \( T \) (Figs. 11–13) curves indicates that the rate of the process is reduced due to internal reasons. In turn, it may be caused by lowering of the rates of crystal nucleation and growth. In view of an ultra-high density of order \( 10^{23} \) m\(^{-3} \) of Al-nanocrystals it has been proposed [25] that the slowing down of the nanocrystallization results from growth limitations which is caused by impingement of the diffusion fields enriched in atoms of TM and RE components rejected from growing nanocrystals. This diffusion-field impingement was detected experimentally in amorphous Al_{87}Ni_{10}Ce_{3} alloy [37] and main efforts have been concentrated on developing of the theoretical approaches to describe this effect [28]. The majority of these models are numerical or semi-quantitative which complicates their using for interpreting of experimental data. On the other hand, it has been shown [25] that the primary crystallization kinetics of amorphous Al_{88}Ni_{7}Y_{5}
alloy may be satisfactory described by using of the exact analytical solution developed by Ham for the growth of the array of precipitation in supersaturated solid solution [38]. However the expressions obtained by Ham are too cumbersome to be used conveniently. In view that the properties of materials with nanocomposite structure are strongly dependent on the size and density of the nanocrystals it is highly desired to develop a relatively simple analytical model to identify the main parameters governing the nanocrystallization process as well as to estimate their values.

In order to simplify description of the diffusion-limited growth of crystals accounting the diffusion fields an attempt to obtain the approximate solution of the problem solved by Ham (Fig. 18) has been recently made [39].

![Diagram](Fig. 18. The schematic representation of the "soft impingement" of growing primary nanocrystals. The symbols on the graph are described in text.)

Similarly to Ham a steady state flux balance equation

$$\frac{dr(t)}{dt} = \left[ \frac{C_i - C_u(t)}{C_i - C_p} \right] \frac{D}{r(t)}, \quad (1)$$

and the conservation of solute law:

$$\frac{4\pi}{3}(C_p - C_i)r^3(t) = \frac{4\pi}{3}r_s^3[C_u(0) - C_u(t)], \quad (2)$$

have been considered. (Here: $C_p$ is the solute concentration in the particle, $C_i$ is the matrix concentration at the particle interface, $C_u(0)$ and $C_u(t)$ are the matrix initial and average concentration as a function of time, respectively; $r(0)$ and $r(t)$ are the initial and time-dependent particle radii, respectively, $2r_s$ is the interparticle spacing , $D$ is the volume diffusion coefficient (Fig. 18)).

Assuming that the effect of diffusion field impingement becomes dominating at the final stage of crystal growth where $C_u(t) \to C_i$ (Fig. 18) the solution of the system of Eqs. (1) and (2) yields the approximate expression of the crystal radius change on time at the final stage of primary crystallization as [39]

$$r(t) = \left[ r^2(0) + (2/3)r_s^2\lambda_i\lambda_S^2\left[1 - \exp\left(-3\lambda_iDt/r_s^2\right)\right]\right]^{1/2}, \quad (3)$$

where $\lambda_i = [(C_u(0) - C_i)/(C_p - C_i)]^{1/3}$.

It should be noted that for the case of free growth of nanocrystals, i.e., $r_s \to \infty$ Eq. (3) transforms into the well-known Zener equation of parabolic growth [40]

$$r_z(t) = \lambda_z\sqrt{Dt}, \quad (4)$$

(with $\lambda_z = [2(C_i - C_u(0))/(C_i - C_p)]^{1/2}$) thus, lending support to the correctness of the analysis.

In view, that even for the case of nanocrystallization the final size of nanocrystals is higher than the critical nucleus radius, $R_n$, Eq. (3) may be further simplified to

$$r_n(t) \approx \sqrt{2/3\lambda_i\lambda_S^2\left[1 - \exp\left(-3\lambda_iDt/r_s^2\right)\right]^2} \quad (5)$$

As can be seen from Fig. 18 the majority of the parameters of Eq. (5) with the exception of $D$ and $C_i$ can be determined from the X-ray diffraction data analysis of the isothermally annealed samples. Taking into
account, that \( r_\theta(t) \) weakly depends on \( C_1 \) and taking the matrix concentration at the particle interface equal 0.25 which corresponds the most typical chemical composition of intermetallic compounds (Al\(_3\)(TM,RE)) a comparison between the experimentally measured and calculated \( L(t) = 2r_\theta(t) \) dependencies provides an opportunity for experimental verification of Eq. (5) as well for estimation of the values of \( D \).

For these purposes the samples of amorphous Al\(_{90}\)Y\(_{10}\) and Al\(_{86}\)Ni\(_6\)Co\(_2\)Gd\(_6\) ribbons have been isothermally annealed for different times at several temperatures and the average sizes of Al-nanocrystals, \( L \), as well as \( r_S \) \( (= [6/(\pi N)]^{1/3}) \) have been evaluated from the X-ray diffraction patterns. Such obtained \( L(t) \) data have then been fitted by Eq. (5) varying the values of \( D \). The results of this analysis are shown in Figures 19 and 20. It can be seen that the calculated \( 2r_\theta(t) \) curves are well approximate the shape of those obtained from the experimental data and within the experimental uncertainty are in good accordance indicating the validity of the proposed model of the growth.

![Fig. 19](image1.png)

Fig. 19. Changes of the average grain size of Al-nanocrystals in amorphous Al\(_{90}\)Y\(_{10}\) alloy at isothermal annealing at 447 (●), 458 (▲) and 487 K (□). The dashed curves were fitted by Eq. (5).

![Fig. 20](image2.png)

Fig. 20. Changes of the average grain size of Al-nanocrystals in amorphous Al\(_{86}\)Ni\(_6\)Co\(_2\)Gd\(_6\) alloy at isothermal annealing at 443 (●) and 473 K (■). The dashed curves were fitted by Eq. (5).

The values of \( D \) for amorphous Al\(_{90}\)Y\(_{10}\) and Al\(_{86}\)Ni\(_6\)Co\(_2\)Gd\(_6\) alloys extracted from this analysis have been approximated by Arrhenius temperature dependencies as shown in Fig. 21. The values of the pre-exponential factor and activation energy estimated from these linearized data yield the following relationships [m\(^2\)/s]: \( D(T) = 573.6 \times \exp (-22965/T) \) and \( D(T) = 2.92 \times 10^{-4} \exp (-17590/T) \) for Al\(_{90}\)Y\(_{10}\) and Al\(_{86}\)Ni\(_6\)Co\(_2\)Gd\(_6\) alloys, respectively. A comparison between these values of \( D \) and the coefficient of self-diffusion of fcc Al [41] shows (Fig. 21) that the effective coefficient of diffusion which governs the growth of Al nanocrystals in amorphous Al\(_{86}\)Ni\(_6\)Co\(_2\)Gd\(_6\) alloy is lower while that in Al\(_{90}\)Y\(_{10}\) alloy is appreciably higher than \( D_{Al} \). The latter result is somewhat unexpected in view of the features of the growth mechanism involving the rejection of the larger atoms of Y from Al nanocrystals. However, on the one hand, it is known that the mobility of atoms in amorphous phases is in general higher than that in crystals [42] and a physical meaning of the effective diffusion coefficients used in the proposed model is not well understood on the other hand. Besides, as it has been shown [43] the tails at the kinetic nanocrystallization curves may be caused not only by soft impingement considered within the presented model, but may be result of branching of Al nanocrystals. So, further investigations are required to provide more convincing evidence for both the validity of the model proposed and the refinement of the parameters.
Another noteworthy feature of the analysis performed is that the activation energy of the effective diffusion coefficient in amorphous Al_{90}Y_{10} alloy (22965 K) coincides with that determined above from the Kissinger analysis (22600 K), Table 1, whereas for Al_{86}Ni_{6}Co_{2}Gd_{6} alloy the activation energy of the diffusivity (17590 K) is only about one-half of that of nanocrystallization (34300 K). This result suggests that the diffusion-limited growth of Al nanocrystals plays the key role in the first crystallization stage of amorphous Al_{90}Y_{10} alloy while nanocrystallization of Al_{86}Ni_{6}Co_{2}Gd_{6} is the more complicated process which the most probably involves nucleation. Note, that this assumption agrees with the results of the nanocrystallization kinetic analysis presented in Section 2.2. In order to clarify the mechanisms of nanocrystallization the theoretical models of kinetics are required and this work is now underway.

### 3. Conclusions

1. Crystallization of a series of 12 binary, ternary, quaternary and quinary amorphous Al_{90...} alloys begins at temperatures 440–584 K by formation of the nanocomposite structures (nanocrystals embedded in the residual amorphous matrix) and occurs in 2 or 3 well-defined stages.

2. The three different nanocrystallization paths at the first crystallization stage have been established including: (1) diffusion limited growth of the quenched-in Al nuclei, (2) nucleation and subsequent diffusion limited growth of Al nanocrystals and (3) nucleation and simultaneous growth of nanoscale crystals of Al and intermetallic compounds.

3. Partial substitution of Gd for Y and (Y + Tb) have no appreciable influence on both thermal stability of amorphous phases and crystallization mechanism while partial replacement of Ni with Co and Fe results in enhancement of the onset crystallization temperature and finally (for proportion 1/3) in change of the nanocrystallization mechanism from primary governed by nucleation and subsequent diffusion limited growth of Al nanocrystals to eutectic-like involving transient nucleation.

4. The activation energies of the first crystallization stage are in the range from 17000 to 65800 K and its values do not correlate with thermal stability of the amorphous phases.

5. The common feature of all kinetic nanocrystallization curves is the tails at high temperature sides of the peaks of the rates of crystallization indicating the retardation of the process due to intrinsic reasons.

6. Formation of nanophase composites having the crystallized volume fractions, the average sizes of Al nanocrystals and the densities in the ranges (0.22–0.59), (14.8–21.0) nm and (1.1–4.3)×10^{23} m^{-3}, respectively, results in essential increasing of the microhardness (by 740–1740 MPa) in comparison with that of amorphous phases.
7. The $H_{\mu}$ values of the nanophase composite structures formed in Al$_{87}$Ni$_8$Y$_5$, Al$_{87}$Ni$_8$Gd$_5$ and Al$_{86}$Ni$_2$Co$_6$Gd$_6$ alloys (5200, 5180 and 5100 MPa, respectively) are close to the highest values reported in the literature.

8. The structural parameters of nanophase composites at the final stage of first crystallization step involving nucleation are dependent on the regime of heat treatment, in particular, isothermal annealing results in enhanced both the volume fraction and density of Al nanocrystals with smaller sizes compared with those obtained at constant rate heating.

9. The second stage of crystallization of amorphous Al$_9$Y$_{10}$ alloy occurs by steady state nucleation and diffusion-limited growth of Al$_3$Y intermetallic crystals and by coarsening of the Al nanocrystals while mechanism of this stage in amorphous Al$_{88}$Ni$_6$Co$_2$Gd$_6$ alloy which results in enlargement of Al nanocrystals sized is debatable.

10. It is established that the changes of the Al nanocrystals sizes in amorphous Al$_9$Y$_{10}$ and Al$_{88}$Ni$_6$Co$_2$Gd$_6$ alloys during isothermal annealing may be satisfactory described within the proposed analytical model assuming retardation of the diffusion-limited growth due to impingement of the diffusion fields.

11. The extracted from the experimental data effective diffusion coefficients governing the growth of nanocrystals in amorphous Al$_{90}$Y$_{10}$ alloy are somewhat lower while those in Al$_{90}$Y$_{10}$ alloy are higher than the self diffusion coefficient of crystalline Al.

12. All studies have been carried out according with the working plan.

4. References


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36. Sahoo K.L., Panda A.K., Das S., Rao V. Crystallization study of amorphous Al_{50}Ni_{5}Mm_{3}Fe_{0.5} alloy by electrical resistivity measurement // Mater. Lett. – 2004. – Vol. 58. – pp. 316–320.

7. List of Symbols, Abbreviations, and Acronyms

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<th>Symbol</th>
<th>Description</th>
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<td>$T_{\text{ons}}$</td>
<td>temperature of transformation onset;</td>
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<td>electrical resistivity</td>
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<td>$H_{\mu}$</td>
<td>microhardness;</td>
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<td>size (diameter) of nanocrystals;</td>
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