Growth kinetics and structure of nanocrystals in Al$_{87}$Ni$_{8}$Y$_{5}$ amorphous alloy

S Mudry, Yu Kulyk
Ivan Franko Lviv National University, Physics of Metals Department, Kyrylo and Mefodii, 8, Lviv, Ukraine.
e-mail: mudry@physics.wups.lviv.ua

Abstract. Al$_{87}$Ni$_{8}$Y$_{5}$ amorphous alloy has been studied by means of X-ray diffraction and X-ray small-angle scattering methods at different temperatures. Scattered intensities and structure factors are analyzed. Structural data are used for calculation of Al-nanocrystals sizes as well as their mean size temperature dependence. X-ray small angle scattering intensities are interpreted by means of Guinier method. Nanocrystall size distribution function and time dependence of mean size of Al-nanocrystals during their growth are obtained.

1. Introduction.
It is known that annealing of amorphous alloys at some definite temperatures allows to obtain the nanocrystalline phases. It is of importance to study the structure of nanocrystals and its change with temperature. Besides, for definition of nanostructure such parameters as nanocrystalline size and their density are used. Generally these parameters are variable and can be described by distribution functions. Nanocrystalline structural units formed in amorphous materials permit to improve the main properties: (mechanical, magnetic, chemical etc.) by controlling the nanocrystals formation process [1,2].

It this work we present the results of X-ray diffraction and X-ray small angle diffraction studies of nanocrystalline structure forming at thermal annealing of Al$_{87}$Ni$_{8}$Y$_{5}$ amorphous alloy. Recently a large attention has been focused on studies of Al-enriched alloys of this system due to considering them as candidate materials in various areas of application: aircraft and space technology, engine construction and machine building industry, electronics and electrotechnical engineering. On that reason more experimental studies of Al-enriched Al-Ni-Y alloys are needed.

2. Experimental
The structural studies were carried out using X-ray diffraction method (diffractometer DRON-3M). Diffraction patterns were obtained by means of high temperature diffractometer which chamber was filled with pure helium in order to avoid the oxidation of samples. Co-K$_\alpha$ radiation, obtained by reflecting from LiF single crystal was used. The penetration width for this radiation was calculated to be equal about $\sim 7$ $\mu$m [3]. The scattered intensities were recorded by electronic system. Scattered intensities obtained at different angles of diffraction were corrected on polarysation and absorption factors taking into account the incoherent scattering [4].

Small angle investigation was carried out using DRON-3M X-ray diffractometer. CuK$_\alpha$-radiation ($\lambda=0.1542$ nm), monochromatized by reflecting from (200) planes of LiF single crystal, has passed
through the specimen. In order to avoid the “parasite” scattering, the slit system was installed before the standard one. Another slit system was installed before detector for reducing of atmospheric scattering. Using the perfect single crystal and collimating of initial and diffracted beams with high accuracy, permitted us to obtain the small angle scattering spectra down to 0.1-0.2 nm\(^{-1}\) value of wave vector. The 0.1 mm slit was installed before detector that allowed us to have the high experimental angular resolution \(\Delta(2\theta) = 0.03^\circ\). Scattered intensities were recoded by scanning within 0.25- 4.00° angle region with 0.05° step and 100 s exposition.

3. Result and discussion.
The structure factors (SF) for Al\(_{87}\)Ni\(_8\)Y\(_5\) amorphous alloy at different temperatures are shown in figure 1. The main feature of these functions is asymmetry of their principal peaks and a shoulder on right hand side. The resolution of this shoulder increases with temperature. In order to interpret the SF we carried out the fitting of experimental maximum profile by Lorentz functions (figure 2). The partial structure functions, corresponding to various structural units, were used to determine such parameters as mean interatomic distances, clusters size and volume fractions of each kind of atomic groups.

![Figure 1. Structure factors of Al\(_{87}\)Ni\(_8\)Y\(_5\) amorphous alloy.](image1)

![Figure 2. Fitting of structure factor.](image2)

The results are listed in table 1.

According to data obtained the structure of Al\(_{87}\)Ni\(_8\)Y\(_5\) amorphous alloy consists of two kind of structural units. Mean interatomic distance in the first of them was found to be close to corresponding parameter for Al (0.286 nm). It allowed us to conclude that atomic arrangement is formed on the base of FCC-cell of Al. Increase of \(r_1\) by 0.003 nm is supposed to be caused by diluting of Y atoms in these atomic groups. The content of Y in Al-based amorphous matrix was estimated using the assumption about linear dependence of interatomic distance on concentration of diluted element. It was found that \(x_Y \approx 7\) at.%. With temperature increase the value of \(r_1\) reduces and that is attributed to rearrangement of Y-atoms in amorphous matrix. The size of structural units decreases with heating also.

| Table 1. Parameters of Al\(_{87}\)Ni\(_8\)Y\(_5\) amorphous alloy structure. |
|-----------------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|
| \(T, K\)       | \(s_1, \text{ nm}^1\) | \(s_2, \text{ nm}^1\) | \(r_1, \text{ nm}\) | \(r_2, \text{ nm}\) | \(L_1, \text{ nm}\) | \(L_2, \text{ nm}\) | \(X_1\) | \(X_2\) |
| 293            | 26.6      | 29.6      | 0.291     | 0.261     | 2.1        | 1.7        | 0.65      | 0.35     |
| 373            | 26.6      | 29.6      | 0.291     | 0.261     | 2.1        | 1.7        | 0.65      | 0.35     |
| 398            | 26.7      | 29.7      | 0.289     | 0.260     | 1.9        | 1.6        | 0.66      | 0.34     |
| 423            | 26.7      | 29.8      | 0.289     | 0.259     | 1.9        | 1.6        | 0.67      | 0.33     |
| 443            | 26.7      | 29.7      | 0.289     | 0.260     | 2.0        | 1.7        | 0.69      | 0.31     |
| 463            | 26.8      | 30.2      | 0.288     | 0.256     | 1.7        | 1.7        | 0.77      | 0.23     |
| 483            | 26.8      | 30.2      | 0.288     | 0.256     | 1.8        | 1.9        | 0.75      | 0.25     |

\(s_1, s_2\)- first and second subpeak positions in SF respectively; \(r_1, r_2\)- corresponding nearest interatomic distances; \(L_1, L_2\)- sizes of first and second kind structural units; \(X_1, X_2\)- their volume fractions.
For the second kind of microgroups of atoms parameter $r_2$ was found to be 0.261 nm and this is significantly less than for previous structural units. This value is close to the sum of atomic radii for Al and Ni (0.268 nm). It allows us to note that shoulder on principal peak in SF corresponds to microgroups, were Al and Ni-atoms are chemically ordered. The content of Al and Ni in these structural units estimated by above mentioned method becomes equal to 22 at.%Al and 8 at.% Ni respectively, that motivated the existence of Al$_3$Ni like structure. Comparing analysis of integral intensities of subpeaks allowed us to calculate the volume fractions of each kind of structural units. As is seen from table 1 the volume of Al-based structural units increases with temperature growth due to partial degradation of Al$_3$Ni–like microgroups.

High temperature X-ray diffraction studies indicate that crystallization of Al$_{87}$Ni$_{8}$Y$_{5}$ amorphous alloy has initial origin that it pronounced in formation of Al nanocrystals from amorphous phase. As is seen from figure 3 where SF for amorphous-crystalline mixture at different temperatures are shown, the heating accompanies by increase of integral intensities and reduction of half height width for diffraction peaks of Al.

![Figure 3. Structure factors for amorphous-crystalline mixture.](image)

In the region of initial crystallization the nanocrystal size increases from 6 nm at T=498 K to 15 nm at T=598 K. Hence, the creation of nanocrystals of Al leads to enriching of amorphous matrix by Ni and Y atoms, which form as result the diffuse regions around the nanocrystals of Al. Since atomic radius of Y (0.180 nm) is larger than one for Al (0.143 nm), the former inhibits the diffusion of Al-atoms, stabilizing in such way the size of nanocrystals [5-7].

In order to determine the other parameters of nanocrystalline structure the analysis of small-angle scattering was carried out. It is shown that nanocrystals of Al make the main contribution into small angle scattering. In quantified way the observed dependence can be described by Guinier formula [8]:

$$I(s) = \sum_k I_k(0) \cdot \exp \left( -\frac{1}{3} \cdot \frac{R_g^2}{s^2} \right);$$

where $R_g$- radius of giration. Values of $R_g$ were calculated with using tangent method [9] and then they were used for estimation of nanocrystals size distribution function [10]:

$$f(R_g) = \frac{2}{\sqrt{\pi}} \cdot \sum_k m_k \cdot \exp \left( -\frac{(R_g - R_{g_k})^2}{R_{g_k}^2} \right);$$

where $m_k = \frac{I_k(0)}{R_{g_k}^3}$ - volume fraction of nanoparticles with $R_{g_k}$ radius.
The distribution functions of Al nanocrystalls sizes (figure 4), calculated from experimental data, show that most probable size of nanocrystals shifts to larger values with increasing of isothermal annealing duration. Using Zener equation [11] for time dependence of nanocrystal size one can write:

\[ D(t) = \lambda \cdot \sqrt{D_v \cdot t} \]

where \( \lambda \approx 1 \) is a parameter that depends on difference between chemical composition of initial nanocrystals and amorphous matrix; \( D_v \) diffusion coefficient, corresponding to temperature of isothermal transformation. Time dependence of mean nanocrystals size is shown in figure 5. Approximation of this dependence by linear function allowed us to calculate the diffusion coefficient at the nuclei-amorphous interface and temperature \( T=493 \) K. This value was founded to be \( D_v = 0.4 \times 10^{-19} \) m\(^2\)/s and confirms that initial crystallization of Al is controlled by diffusion of Y-atoms.

4. Conclusions

The structure of Al\(_{87}\)Ni\(_{8}\)Y\(_5\) amorphous alloy is inhomogeneous in wide temperature range up to crystallization point. Main structural units are Al(Y) solution and Al\(_3\)Ni-like chemical ordered microgroups. The fraction of former increases with temperature whereas the fraction of the last decreases.

Time dependence of nanocrystall mean size shows the linear behavior and allows to determine the diffusion coefficient in nuclei-amorphous interface, which was found to be \( D_v = 0.4 \times 10^{-19} \) m\(^2\)/s at \( T=493 \) K. Diffusive layers of Y-atoms around the nanocrystals are responsible for growths process mainly.

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