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Modification of the Atomic Structure of liquid $Al_{0.973}Ni_{0.027}$ Eutectic Alloy by Carbon Nanotubes

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The short-range order structure of the liquid $Al_{0.973}Ni_{0.027}$ eutectic alloy and eutectic based composites with carbon nanotubes containing 5, 10 and 15 % was investigated. The changes of the main structure parameters (interatomic distances, coordination numbers, cluster sizes) was analyzed depending on the nanotubes content and temperature of the composites. As a result of the addition of carbon nanotubes, the atomic structure contracting of the liquid $Al_{0.973}Ni_{0.027}$ eutectic was revealed.

Keywords: short-range order structure, composites, carbon nanotubes, aluminum alloys.

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Introduction

The necessity to obtain light and durable materials arose primarily with the development of aircraft and aerospace industries and remains relevant to this day. It is known that as the strength and stiffness of the materials increases, the dimensions and accordingly the mass of the material of the vehicle decreases. This promotes to increase the load capacity and reduce the amount of fuel used by aircraft and cars. It is known that metals and alloys cannot have high strength and stiffness values at the same time, which has led to intensive studies of composite materials. In these materials, strength and ductility are provided by a metal matrix and stiffness by filler.

Due to their mechanical, electrical and thermal properties, carbon nanotubes (CNTs) are promising reinforcing materials in composites. In particular, as has been shown experimentally and by computer simulation methods, carbon nanotubes have extremely high values of Young's modulus (> 1 TPa) and strength (about 100 GPa) [1-3]. One way of using these properties of nanotubes is materials strengthening, thus forming composites. The best candidates for this are metals and metal alloys that combine high ductility with durability.

Currently, there are many works describing methods for producing metal matrix composites reinforced with carbon nanotubes [4–7]. The most common of these are powder metallurgy techniques, liquid state mixing methods, high temperature metal deposition and electrochemical methods. Less common but effective methods for producing composites are atomic-level mixing and gas-phase chemical deposition.

Several methods have been developed for the uniform distribution of carbon nanotubes in a metal matrix. The first was the method of mixing metal powders with nanotubes in ball mills. But, as it was shown, in the process of such mixing nanotubes are destroyed, which degrades the mechanical properties of the composite [8]. Molecular mixing methods lead to the contamination with oxides due to incomplete reduction of powders, whereas the dispersion is very good. Other methods that enable the dispersion of nanotubes in a metal matrix are gas phase deposition and electrochemical methods.

Today, there are already works that describe the results of studies of the mechanical properties of metal matrix composites strengthened with carbon nanotubes [9-12]. However, there are still many unexplained and incompletely studied problems concerning the dispersion of nanotubes in a metal matrix and surface phenomena on the boundary of a carbon nanotube-metal. As far as the process of obtaining composites is often carried out by liquid-phase sintering, issues of interaction of carbon nanotubes with a liquid matrix deserve special attention.

Therefore, the purpose of this work is to synthesize

dispersed metal composites strengthened with carbon nanotubes and to study the structure of such solid-liquid composites. The eutectic $Al_{0.973}Ni_{0.027}$ alloy, which has been used in the industry for a long time, but also requires improved performance, was chosen as the matrix.

I. Experimental methods

Synthesis of metal matrix composites strengthened with carbon nanotubes was carried out by electroplating of nanotubes with nickel, followed by mixing of coated nanotubes with high purity aluminum powder. Further treatment of the composites was carried out by powder metallurgy route and liquid-phase sintering. The thermodynamic and kinetic conditions of composite formation were controlled by varying the composite temperature and mixing time.

The microstructure of the composites was examined by scanning electron microscopy in the secondary electrons.

The structure in the liquid state was investigated by high-temperature X-ray diffractometry, which made it possible to obtain the X-ray diffraction patterns at different temperatures up to 1600 K. The geometry of an incident X-ray beam, a center of the camera, and an inlet slit of the detector, corresponded to the Bragg-Brentano type focusing geometry [13]. The accuracy of the measurement of the X-ray intensity was in the range of 2 - 3 %. The temperature was measured and maintained with an accuracy of ± 2 K.

The obtained experimental angular dependences of the intensity of the diffracted radiation were corrected for polarization, absorption, and anomalous dispersion [14]. Normalization to electron units was carried out using the method described in [15]. Corrected and normalized X-ray diffraction curves were used to calculate structure factors (SF), pair correlation functions (PCF), and radial distribution functions of atoms which in turn were used to determine the main structure parameters.

II. Results and Discussion

The morphology of uncoated and nickel-coated nanotubes is shown in Figure 1 (a, b), from which regions of metallic nickel in the nanotube array are clearly visible. To confirm the presence of nickel on the surface of the nanotubes, an X-ray phase analysis of the

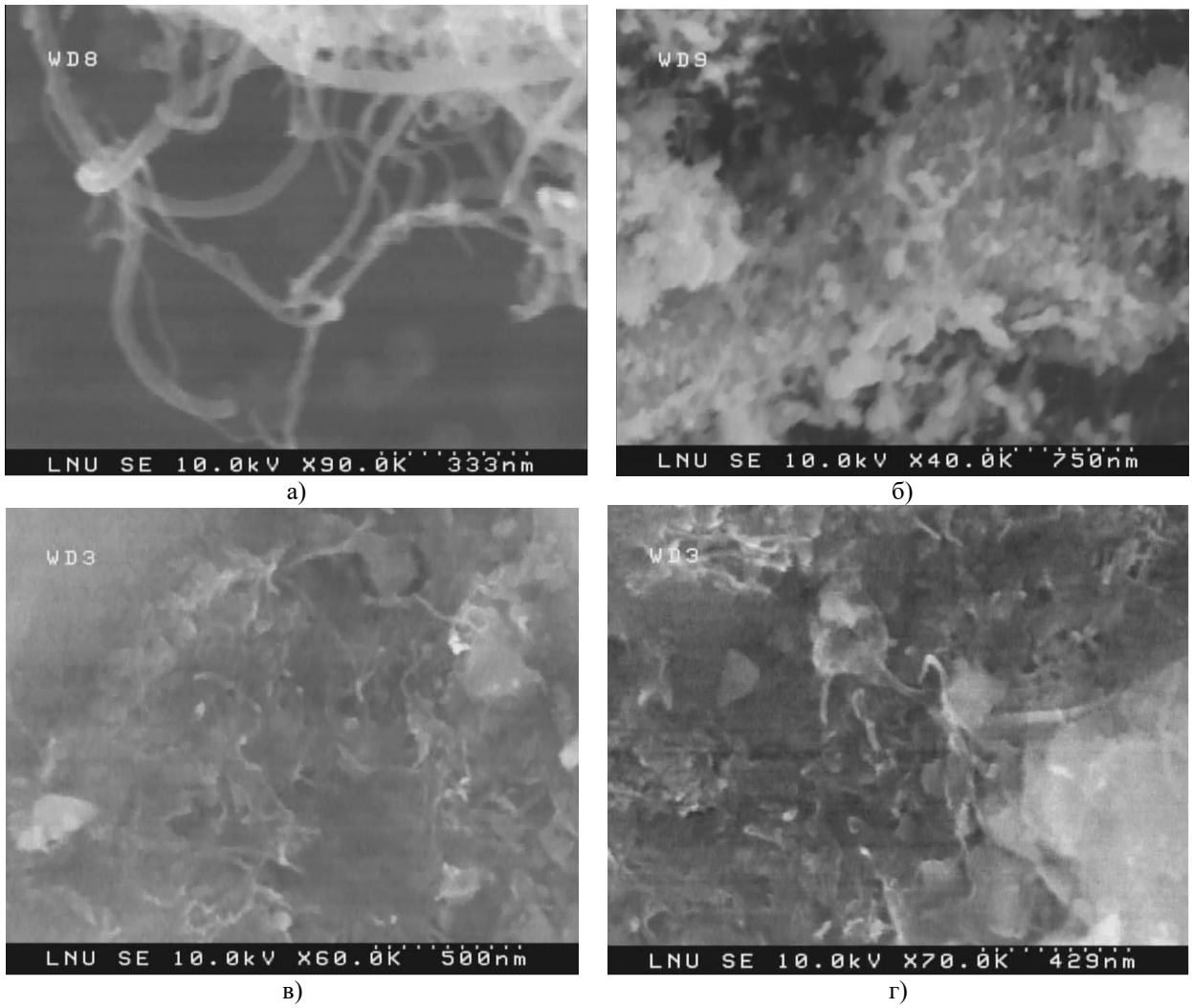

Fig. 1. The morphology of untreated carbon nanotubes (a) coated with nickel (b), as well as the microstructure of $Al_{0.973}Ni_{0.027}$-CNT composites with the content of nanotubes 10 (a) and 15 (b) vol.%.

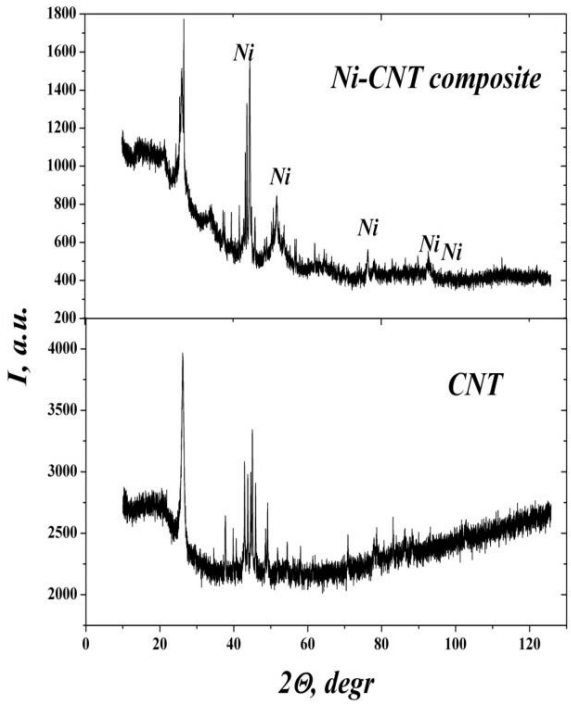

Fig. 2. Diffraction patterns of untreated carbon nanotubes and nickel coated.

Ni-CNT composite was performed (Fig. 2), which revealed the presence of diffraction peaks corresponding to crystalline nickel. As a result of liquid-phase sintering, composites with uniform nanotube distribution in the sample volume were obtained (Fig. 1 c, d).

The study of composites structure obtained by the liquid phase sintering method in the liquid state was carried out by analyzing structure factors (Fig. 3), pair correlation functions and parameters obtained from them. As can be seen from Figure 3, the main feature of the structure factors of the composite in comparison with the eutectic is an increase in the width of the first maximum, a decrease in its height (Fig. 4) and an increase in the degree of asymmetry. In addition, as the nanotube content increases, the position of the first maximum of the structure factors shifts toward greate wave vectors (Fig. 5).

The decrease in the height of the first maximum of the structure factor indicates a decrease in packing density due to the influence of carbon nanotubes on the structure of the eutectic. In turn, the width of the first maximum of the structure factor is related to the size of the melt clusters. Using this parameter, the temperature dependences of the clusters size of molten $Al_{0.973}Ni_{0.027}$ eutectic with different nanotube contents were calculated (Fig. 6).

As can be seen from this figure, an increase in the content of nanotubes leads to a decrease in the size of the cluster throughout the temperature interval in which the study was conducted. At the same time, there is a minimum on the temperature dependence of the cluster sizes, which at higher nanotube contents shifts towards higher temperatures. The increase in the size of the cluster at a certain temperature can be explained by the supposition of intensification of the diffusion processes

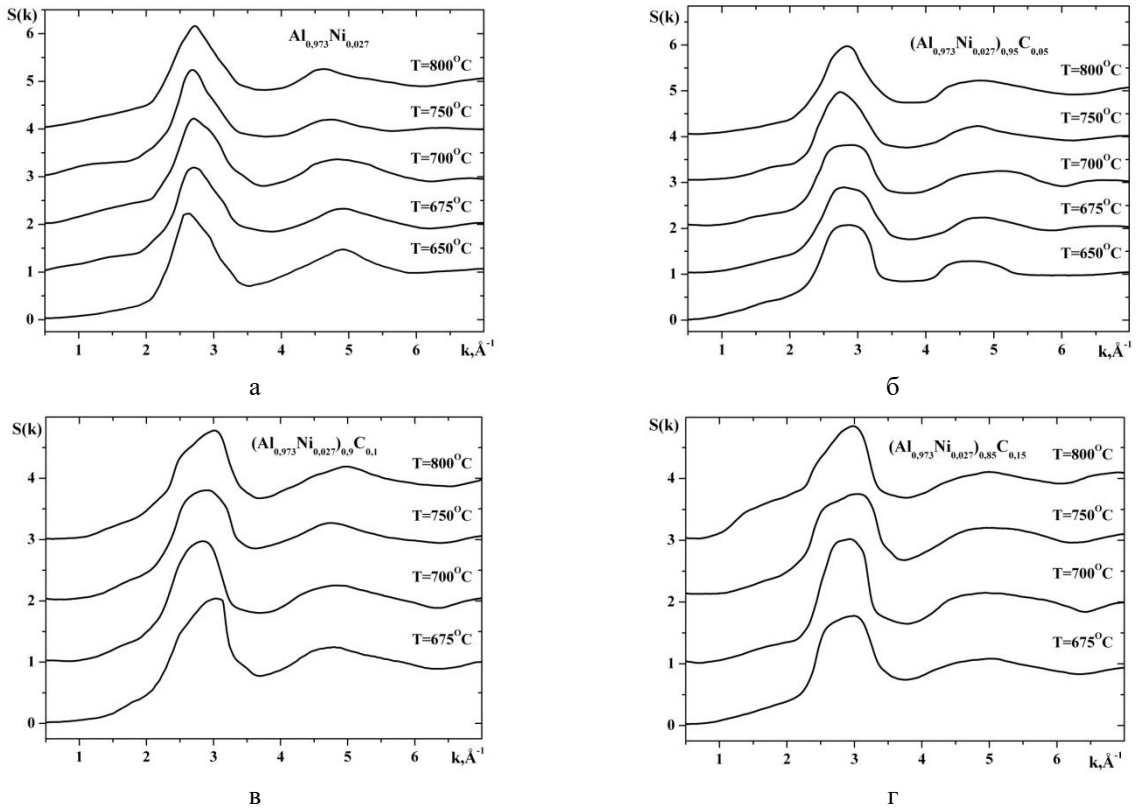

Fig. 3. Structural factors for eutectic $Al_{0.973}Ni_{0.027}$ and nanotubes containing Al-Ni-CNT composites 5, 10 and 15 vol.%.

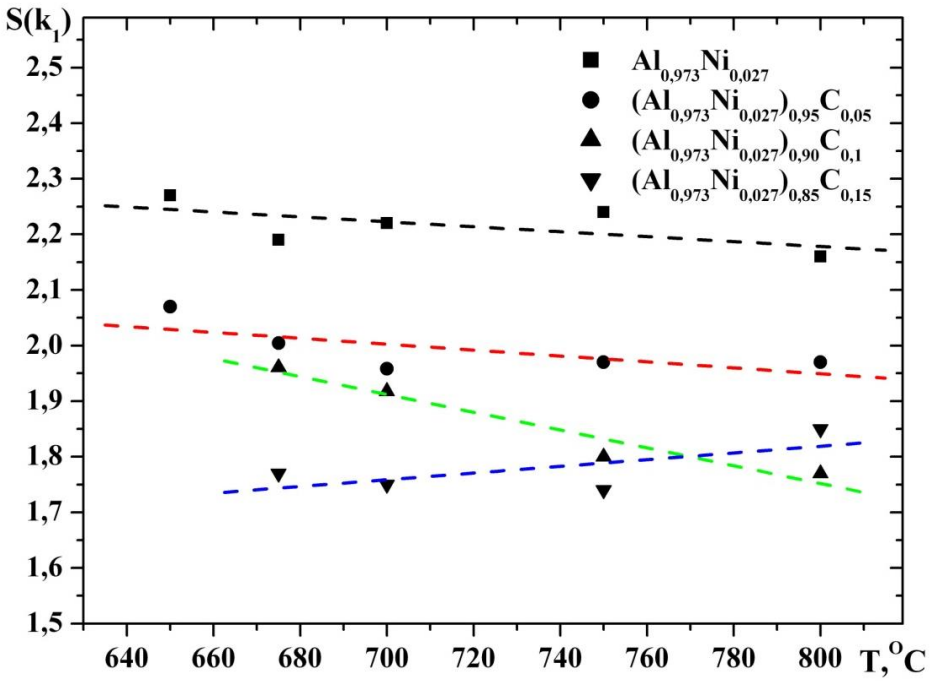

Fig. 4. Temperature dependence of the height of the first maximum of the structural factor of Al-Ni-CNT composites.

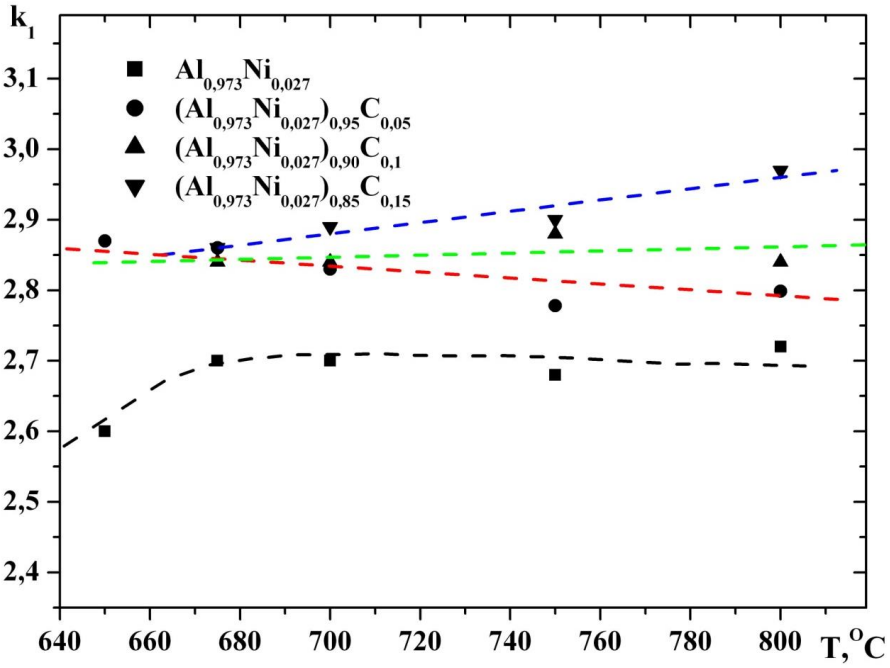

Fig. 5. Temperature dependence of the position of the first maximum of the structural factor of composites Al-Ni-CNT.

and the decrease in the inhibitory effect of the nanotubes by the diffusion processes. It is clear that increasing the content of nanotubes leads to an increase in the temperature of the diffusion barrier.

The addition of nanotubes to the $Al_{0.973}Ni_{0.027}$ eutectic also causes the reduction of the most probable interatomic distances, which indicates the contraction of the short-order structure within the first coordination sphere. Taking into account the previously mentioned fact of reduction of the packing density, we can assume that the main contribution to its reduction is made by nanotubes due to the presence of cavities.

Along with the reduction of the most probable distances, there is a significant decrease in the radius of the second coordination sphere while increasing the content of carbon nanotubes (Fig. 7). This indicates to the contracting of the short-range order structure not only within the first coordination sphere, but also over longer

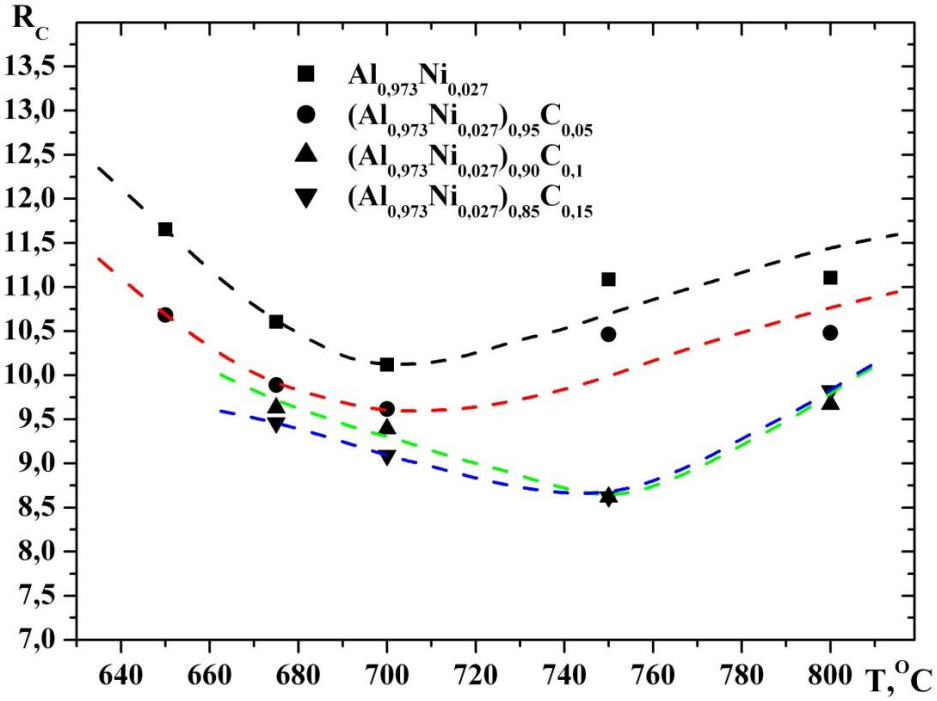

Fig. 6. Temperature dependences of the size of molten eutectic clusters $Al_{0.973}Ni_{0.027}$ with different contents of nanotubes.

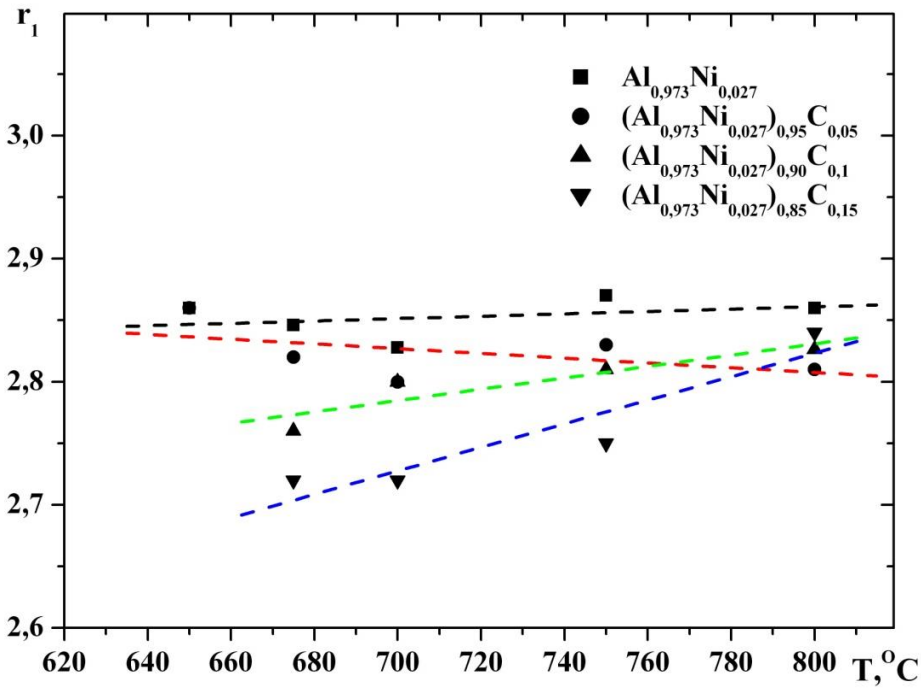

Fig. 7. Temperature dependence of the most probable interatomic distances of the composite $Al_{0.973}Ni_{0.027}$-CNT.

distances.

At the same time as the most probable interatomic distances decrease, the coordination number increases. This fact reaffirms the hypothesis of the contracting of the short-range structure within the first coordination sphere.

Given the described transformation of the short-range structure, one can make certain assumptions about the nearest atomic environment of carbon nanotubes in a liquid matrix. Since, as it has been shown that the addition of nanotubes mainly affects the compaction of the structure within the first and second coordination spheres, as well as the decreasing of clusters size we can assume that the nanotubes are located mainly at the boundaries of the clusters in intercluster regions with smaller atomic density.

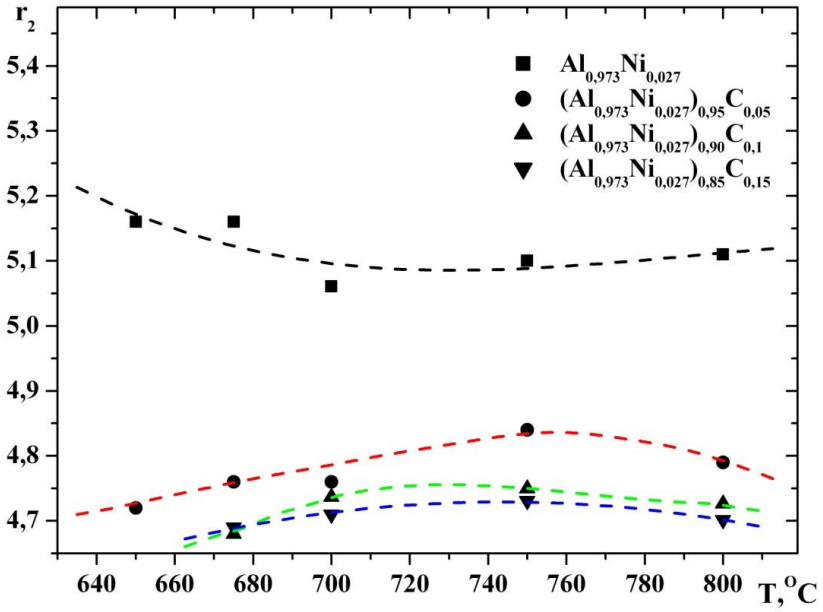

Fig. 8. The temperature dependence of the radius of the second coordination sphere of the molten matrix composite $Al_{0.973}Ni_{0.027}$-CNT.

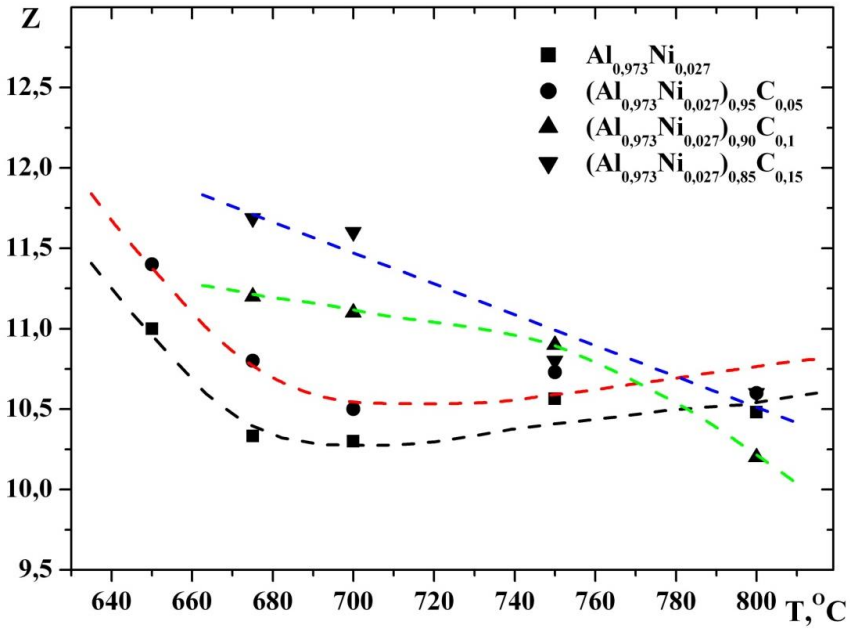

Fig. 9. Dependence of coordination number of composite $Al_{0.973}Ni_{0.027}$-CNT on temperature.

Conclusions

As a result of X-ray diffraction studies of liquid $Al_{0.973}Ni_{0.027}$ eutectic based composites with carbon nanotubes and analysis of the profile of the structure factor main maxima, a decrease in the packing density and the size of the melt clusters are revealed while the content of carbon nanotubes increases.

The decrease in the most probable interatomic distances, the radius of the second coordination sphere of the molten eutectic matrix, and the increase in coordination numbers testify to the contracting of the short-range order structure which is caused by the presence of nanotubes due to the presence of cavities in them.

Considering the changes in the main structure parameters, it has been suggested that carbon nanotubes are allocated in the intercluster regions of the molten matrix, affecting its size and structure.

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Модифікація атомної структури рідкої евтектики $Al_{0.973}Ni_{0.027}$ карбоновими нанотрубками

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Досліджено структуру ближнього порядку рідкої евтектики $Al_{0.973}Ni_{0.027}$ та композитів на її основі з вмістом карбонових нанотрубок 5, 10 та 15 об.%. Проаналізовано зміну основних структурних параметрів (міжатомних відстаней, координаційних чисел, розмірів кластера) залежно від вмісту нанотрубок та температури композитів. Виявлено, що в результаті додавання карбонових нанотрубок відбувається ущільнення атомної структури рідкої евтектики $Al_{0.973}Ni_{0.027}$.

Ключові слова: структура ближнього порядку, композити, карбонові нанотрубки, алюмінієві сплави.