Intensive Plastic Deformation Influence on Phase Relations of Cobalt Nanocrystals

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The choice of cobalt as an object of study is due to the fact that it is characterized by a low temperature of polymorphic transformation. This makes it possible to use it as a model material for studying the effect of crystallite sizes on the nature of these transitions and phase composition. Nanostructured samples of cobalt were obtained by the method of intense plastic deformation by torsion. High quasi-hydrostatic pressure in the working area up to 8 GPa was created on a Bridgman anvil-type installation. Anvils were made of tungsten carbide. The method allows to obtain samples of high purity without pores and impurities. X-ray diffraction studies were carried out on a DRON-7 diffractometer with cobalt radiation. X-ray analysis was performed according to the Bragg-Brentano method. To conduct phase analysis, Kα lines were used at a scan step of 0.04 degrees, and when analyzing the profile of diffraction lines and determining their width – at 0.01 degrees. The absolute error in measuring the angular positions of diffraction maxima did not exceed ± 0.020. The size of cobalt nanocrystallites reached about 25-50 nm. It is established that during low-temperature annealing recovery occurs in the structure of cobalt. Annealing above 300 °C leads to the recrystallization of its structure. The nanocrystalline cobalt obtained by intense plastic torsion deformation after heating above the phase transition temperature and cooling below this temperature retains the high-temperature fcc structure. It is shown that the nature of the fcc-hcp transition delay can be associated with changes in the size and strained state of crystallites forming nanocrystalline cobalt. All of the above confirms the relevance of our research.

Keywords: Cobalt, Severe plastic deformation, Nanostructure, Bragg-Brentano method, Annealing, Recovery, Recrystallization, Structural transformations.

1. INTRODUCTION

Nanocrystalline (NC) materials are of great scientific and practical interest because of their unusual physical properties [1-6]. With the transition to the NC state, the diffusion coefficient increases by several orders of magnitude compared with other materials [7-11], chemical activity increases, an abnormal Curie temperature, saturation magnetization, elastic properties [12] are observed as well as the change in electrical resistance and other characteristics of materials [13]. At the same time, NC materials are not thermally stable. When heated, relaxation processes develop in such materials leading to a gradual transition to a macrocrystalline state and loss of physical properties due to the NC structure [14, 15]. The results of recent studies suggest that the special properties of NC materials are caused not only by the large length of the internal interfaces, but also by the special non-equilibrium state of the grain boundaries. Therefore, the understanding of the behavior peculiarities of NC materials is closely related to the understanding of the physical nature of the non-equilibrium internal boundaries [16].

It is currently considered that the physical properties of NC materials are due to the large contribution of grain boundaries and elastic stresses in the crystal lattice [17]. For each material there is a characteristic critical size of the structural unit, below which the physical properties of the material vary radically. When crystallite sizes are smaller than the critical size, dislocations and vacancies are pushed out of the crystal volume into the grain boundary region. With a decrease in crystallite size in a number of materials, a change in the type of crystal lattice is observed. The lattice parameters with decreasing crystallite sizes for different materials often change ambiguously. The change in chemical and physical properties with the transition to the NC state is largely explanatory [18]. However, the nature of many phenomena occurring in NC materials has not been studied enough. Therefore, the study of the nature of processes in NC materials is of great scientific and practical interest.

The interest in the problem of the stability of NC materials obtained by severe plastic deformation (SPD) is associated with their practical application. As a rule, research in this area is aimed at stabilizing the structure of NC materials to higher temperatures. For example, it is known that the NC structure can be stabilized by adding a small amount of the corresponding phase. It is well known that the thermal stability of NC copper can be improved by adding a certain concentration of aluminum oxide Al_2O_3 [19].

This paper discusses the results of the study of phase and structural transformations in NC cobalt obtained by SPD. The choice of cobalt as an object of research is due to the following reasons:

• Cobalt can be obtained in the NC state by the SPD method.

• Cobalt has a relatively low polymorphic transformation temperature (~ 427 °C) from a hexagonal close-packed (hcp) structure to a cubic face-centered structure

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(fcc), therefore it is a convenient model object for studying the influence of crystallite sizes and their strained state on the nature of such transitions. NC cobalt has a complex phase composition, exhibits anomalous magnetic properties and is characterized by thermal expansion. All this together determines the relevance of the research undertaken in this work.

Macro-crystalline cobalt at room temperature has an hcp structure. At temperatures of the order of (417-427) °C, cobalt transforms from the hcp structure into the fcc structure. This transition is a diffusionless reversible martensitic-type phase transition. Depending on the content of impurities, defect concentration, heating and cooling rates, degree of deformation and other factors, this transition is characterized by a hysteresis, the width of which reaches approximately 40 °C. It has been established that one of the main factors affecting the stability of phases and phase transition is the grain size. At small grain sizes, the fcc phase of cobalt is stable, while at room temperatures, the hcp structure is mainly formed in macro-crystalline materials. In samples with an inhomogeneous grain size distribution, a mixture of fcc and hcp phases is formed. However, to date, the influence of grain size and the associated lattice micro-distortion on the stability of the cobalt phases has not been studied enough. The study of the structure and physical properties of NC cobalt obtained by SPD torsion is also devoted to a small number of works. When SPD, cobalt torsion forms a hcp structure with a grain size of about 100 nm.

2. EXPERIMENTAL TECHNIQUE

To obtain nanostructured cobalt samples in this work, the method of SPD by torsion was used under high quasi-hydrostatic pressure on a Bridgman anvil-type installation. Unlike the powder compaction technique and the ball grinding method, this nanostructuring method allows obtaining samples without pores and impurities. The installation consists of two anvils mounted on a hydraulic press. The press allows to create pressure in the working area up to 8 GPa. Anvils are made of tungsten carbide. The lower anvil is movable and can rotate around a vertical axis relative to the upper one.

X-ray studies were performed on a DRON-7 diffractometer on Co-radiation using the Bragg-Brentano method. Fe-filter was applied to suppress the Kβ-line. A scintillation counter was used as a detector. Diffraction patterns were taken at an anode voltage $U = 40$ kV and an anode current $I = 20$ mA. To conduct phase analysis Kα-lines were used. The survey was carried out by the step method by dialing the number of pulses during the exposure time $t = 5$ s. When conducting phase analysis, the scanning step was 0.04 degrees, and when analyzing the profile of diffraction lines and determining their width – 0.01 degrees. The absolute error in measuring the angular positions of the diffraction maxima did not exceed ± 0.02°. The basic hardware error in measuring the pulse counting rate did not exceed 0.35 %. For phase analysis, the following slits on the primary beam were used: the horizontal slit – 8 mm, the vertical slit – 2 mm; on a diffracted beam: horizontal slit – 8 mm, vertical slit – 0.1 mm. Soller's gaps on the primary and

diffracted beam had a divergence of 1.5°.

In this study, the diffraction patterns were taken from the flat surface of the sample at room temperature. Samples obtained after plastic deformation by torsion under pressure had the form of disks. Interplanar distances were determined by measuring the corresponding diffraction angles using the Wolf-Bragg formula:

$$2d_{hkl}\sin\theta = n\lambda,$$

where λ is the X-ray wavelength, θ is the angle of reflection, d_{hkl} is the interplanar distance, n is the order of reflection. The lattice parameters a and c were determined using a formula with known indexes of planes (hkl) by the least squares method using a computer program:

$$\frac{1}{d^2} = \frac{4}{3a^2}\left(h^2 + hk + k^2\right) + \frac{l^2}{c^2}.$$

3. RESULTS AND DISCUSSION

3.1 Annealing Temperature Influence on the Cobalt Microstructure

To solve these problems, we carried out electron microscopic studies. Fig. 1a shows the microstructure of a plastically deformed sample before annealing. It can be seen that the microstructure of the sample after plastic deformation is fairly uniform; the boundaries between the crystallites are indistinct, blurred. The average crystallite size is hardly determined and is about 25-50 nm. The diffraction pattern of the sample consists of a set of reflections closely spaced around the circumference, which indicates a small crystallite size and the size uniformity. The marked elongation of reflexes in the azimuthal direction indicates a high level of internal stresses. After annealing at 300 °C, crystallite sizes almost did not change, but the boundaries between them became clearer (Fig. 1b). This indicates that a partial recovery has occurred in the sample.
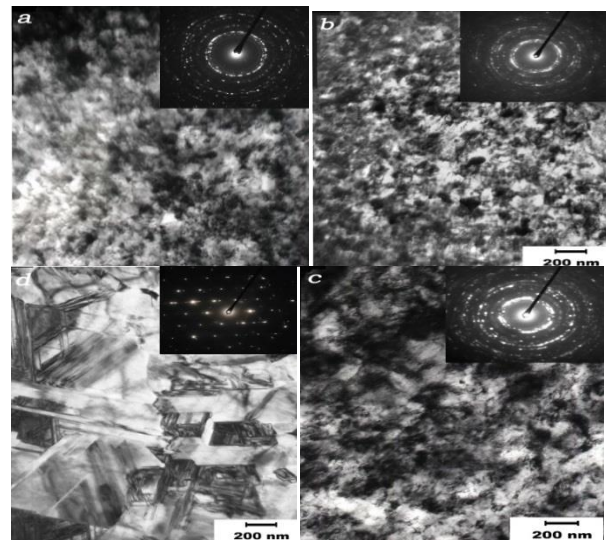
Fig. 1 – Cobalt microstructure after plastic deformation (a) and annealing at temperatures of 300 °C (b), 400 °C (c) and 500 °C (d)
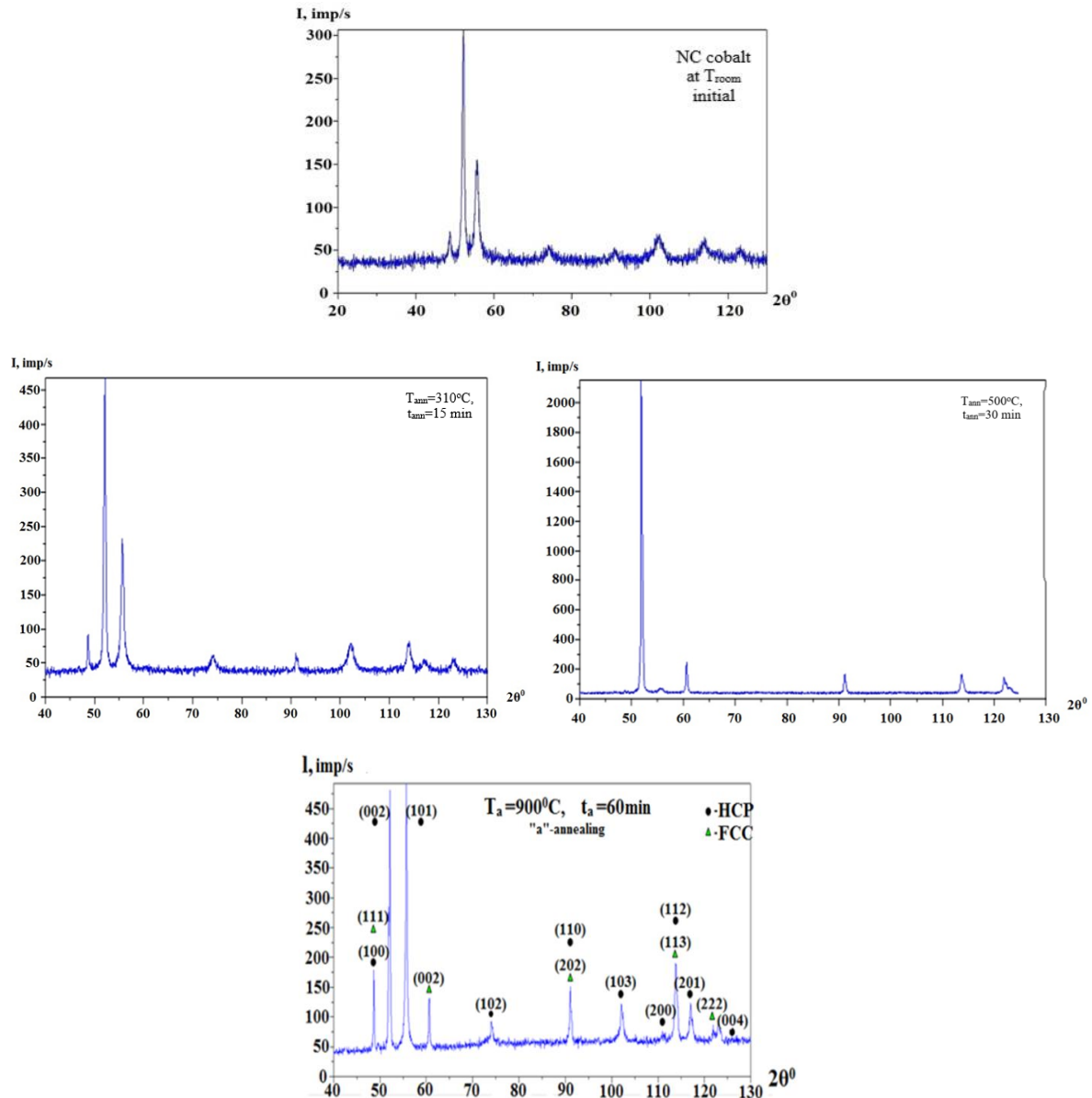
Fig. 2 – Diffraction patterns of NC cobalt annealed at different temperatures

The diffraction pattern of the sample after annealing at 300 °C has noticeably changed: the intensity of individual reflexes has increased and the number of reflexes on the rings has noticeably decreased. This indicates an increase in the size of crystallites and a decrease in their number in the irradiated volume. The elongation of reflexes in the azimuthal direction indicates the preservation of internal stresses in the crystallites. Thus, after annealing at temperatures of about 300 °C, in the sample recovery takes place and recrystallization begins. After annealing at 400 °C, the crystallite size increases noticeably, the boundaries be-tween them remain blurred (Fig. 1c). With an increase in the annealing temperature, the intensity of individual reflexes continues to grow, indicating a continuation of the crystallite sizes growth. After annealing at 500 °C, the process of primary recrystallization in the sample is completed (see Fig. 1d).

Therefore, according to the results of electron micro-

scopic studies of the structure of cobalt, we can draw the following conclusions:

· In NC cobalt obtained by SPD torsion, crystallite sizes are approximately 25-50 nm.

· At annealing temperatures of up to ~ 300 °C, in NC cobalt recovery is observed, and above 300 °C – recrystallization occurs.

3.2 Determination of the Samples Phase Composition

Nevertheless, according to the results of electron microscopic studies, it is difficult to judge the change in the phase composition of the samples and the crystallite size during annealing. Therefore, it is of interest to determine the phase composition of the samples, the sizes of structural fragments and their changes in the annealing process by using other, more informative methods. Based on this, additional studies have been conducted on the influ-

ence of SPD and annealing for the phase composition of cobalt nanocrystals by measuring diffraction patterns. Fig. 2 shows the diffraction patterns of NC cobalt obtained by SPD torsion and samples annealed at different temperatures. Diffraction patterns were obtained at room temperature from the flat surface of the sample formed as a result of SPD torsion. To eliminate the effects of quenching, during annealing above the fcc-hcp phase transition temperature, samples up to 300 °C were cooled with a furnace at a rate of ~ 100 deg/h and then in air. It can be seen from the figure that plastically deformed cobalt, like undeformed, has an hcp structure at room temperature. Therefore, plastic deformation does not lead to a change in the type of crystal lattice of cobalt. Fig. 2 also shows that the plastically deformed samples, annealed at temperatures up to 450 °C, also have an hcp structure. Depending on various factors, cobalt undergoes an fcc-hcp phase transition during heating in the range of 422-440 °C, while cooling – in the range of 387-405 °C. It follows from this that plastic deformation does not lead to a noticeable decrease in the temperature of the polymorphic fcc-hcp transition of cobalt.

Further, the sample after annealing at 500 °C and subsequent cooling to room temperature mainly consists of the fcc phase. Thus, plastically deformed cobalt after annealing above the temperature of the hcp-fcc transformation and subsequent cooling below this temperature retains the structure of the high-temperature fcc phase. Plastic deformation prevents the transition of the high-temperature fcc phase of cobalt to the low-temperature hcp phase during its cooling. Samples annealed at temperatures from 600 °C to 900 °C at room temperature consist of a mixture of the low-temperature hcp phase and the high-temperature fcc phase.

The nature of the fcc-hcp transition delay can be related to changes in the size and strained state of the crystallites. During plastic deformation, the crystallite sizes decrease, and strong distortions appear in the crystal lattice. In the volume of crystallites, lattice distortions can be caused by dislocations and point defects. In addition, during plastic deformation, a developed grain-boundary region is formed with a strong defect structure, which may still contain an amorphous phase. Lattice distortions lead to a decrease in the packing density and to an increase in the elastic energy compared with the density and energy of the ideal lattice. The relative contribution of distorted regions to the crystal energy increases with decreasing crystallite size. Therefore, in cobalt crystallites, whose dimensions are smaller than the critical one, the formation of an fcc structure with a denser packing is more advantageous. Above the temperature of the hcp-fcc transition, the cobalt-type nanocrystals have an fcc structure. During annealing, some crystallites of the fcc phase grow to a critical size and, when cooled below the fcc-hcp transition temperature, acquire the hcp phase. Thus, according to the results of X-ray phase analysis, the following conclusions can be made:

• plastically deformed cobalt at room temperature retains its hcp structure;

• NC cobalt, obtained by SPD torsion, after heating above the phase transition temperature and cooling below this temperature, retains the high-temperature fcc structure. The NC structure of cobalt, obtained by SPD, prevents the transition of the high-temperature

fcc phase of cobalt to the low-temperature hcp phase during its cooling.

3.3 Annealing Temperature Influence on the Lattice Parameters

To confirm the above assumptions about the stability of the hcp and fcc phases of NC cobalt, the lattice parameters of the cobalt nanocrystals were studied as a function of the annealing temperature. It is known that the characteristics of the lattice are structurally sensitive parameters. Therefore, the study of the influence of cobalt crystallite sizes on lattice periods is important for understanding the structural changes occurring in the material. At room temperature, the NC cobalt, according to our data, has a hexagonal structure with the following lattice parameters: $a = 2.509$ Å and $c = 4.067$ Å. Fig. 3 and Fig. 4 show respectively the dependences of the lattice parameters and the volume of the unit cell of the hcp NC cobalt on the annealing temperature. Within the limits of measurement errors, the parameter a does not change up to the annealing temperature $T = 200$ °C. The average value of the parameter $a = 2.508$ Å in this temperature range is higher than the parameter a for macrocrystalline undeformed cobalt. At annealing tempera-
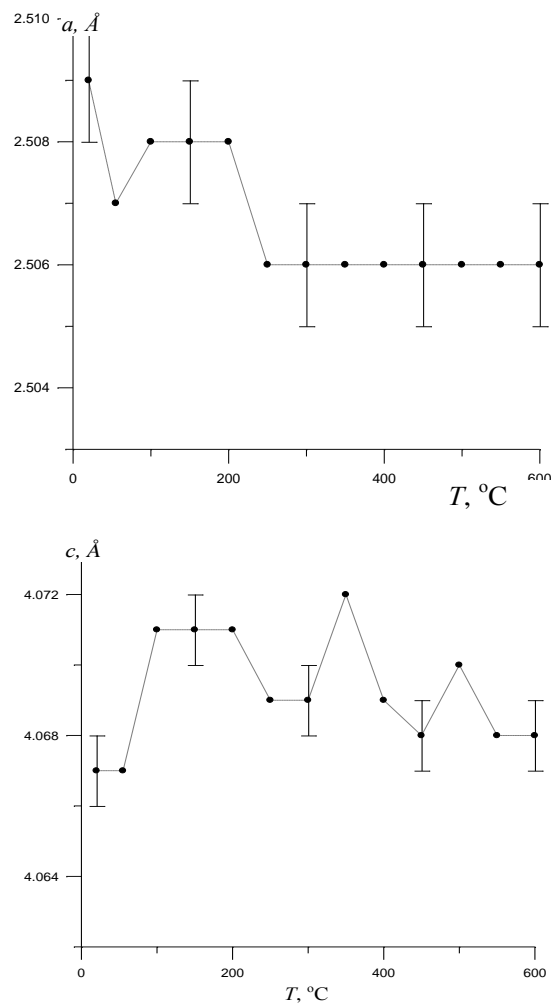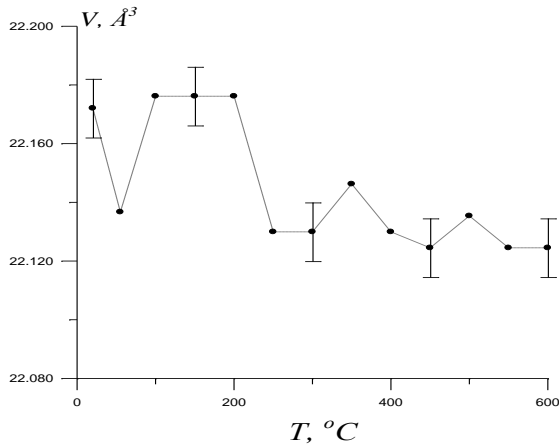

Fig. 3 – Dependence of the lattice parameters a and c of NC cobalt on annealing temperature

Fig. 4 – Dependence of the unit cell volume of NC cobalt on the annealing temperature

tures above $T = 200$ °C, the parameter a decreases to $a = 2.506$ Å. This value of the parameter a almost coincides with the lattice parameter for the macrocrystalline undeformed cobalt $a = 2.505$ Å. At annealing temperatures above $T = 250$ °C, the lattice parameter a does not change within the limits of measurement accuracy.

During plastic deformation, a crystallographic texture forms in cobalt without changing the type of crystal lattice. Often in metals with a hcp structure, during plastic deformation, the basic planes are oriented predominantly perpendicular to the direction of the applied load. In this case, the parameter c should decrease somewhat in comparison with the parameter c of the undeformed sample, and the parameter a should increase. During annealing, the concentration of defects in the crystallites decreases, and the lattice parameter a takes on a value close to the parameter of the defect-free crystal.

After annealing at $T = 100$ °C, the lattice parameter c increases to $c = 4.071$ Å. This value of the parameter c is lower than the parameter c for macrocrystalline undeformed cobalt with $c = 4.089$ Å. After annealing at a temperature $T = 200$ °C, a noticeable decrease in the parameter c is observed. The parameter c decrease correlates with the parameter a and the volume of the unit cell V (Fig. 4). These results confirm our assumptions that, at a temperature $T \sim 200$ °C, active relaxation processes begin, which lead to a decrease in the concentration of lattice defects. The jump in the $C(T)$ and $V(T)$ dependences at $T = 350$ °C is associated with the beginning of the recrystallization process. Because the relative change in volume after recovery is $\Delta V/V = 0.20$ %, and the lattice parameters are $\Delta a/a = 0.12$ % and $\Delta c/c = 0.04$ %.

To confirm our assumptions about the stability of the hcp and fcc phases of NC cobalt, we studied the dependence of the ratio of the parameters c/a on the annealing temperature (Fig. 5). For non-annealed NC cobalt, the ratio is $c/a = 1.621$, which is noticeably less than the value of this parameter for macrocrystalline undeformed cobalt (c/a) MC $= 1.632$ and the theoretical value of this parameter (c/a) $T = 1.633$, corresponding to the most stable state of the hcp structure. Consequently, the hcp phase of NC cobalt obtained by SPD torsion is less stable than the hcp phase of macrocrystalline undeformed cobalt. With an increase in the annealing temperature

for NC cobalt, the ratio of the parameters (c/a) increases to the value $(c/a) = 1.6233$. Consequently, the hcp phase of NC cobalt with increasing annealing temperature becomes more stable.

For ideal hcp and fcc structures, the packing densities are the same and the crystal energies are close. At the same time, for NC cobalt obtained by SPD torsion, the packing density is lower than for an ideal hcp structure. Therefore, the most close-packed fcc structure with a lower crystal energy should be realized in NC cobalt. During annealing of cobalt nanocrystals, the density of defects in the material decreases, and the packing density tends to the density of an ideal hcp structure. This leads to a decrease in the elastic energy of the hcp lattice, due to which the transition of the fcc structure into the hcp structure becomes more probable.
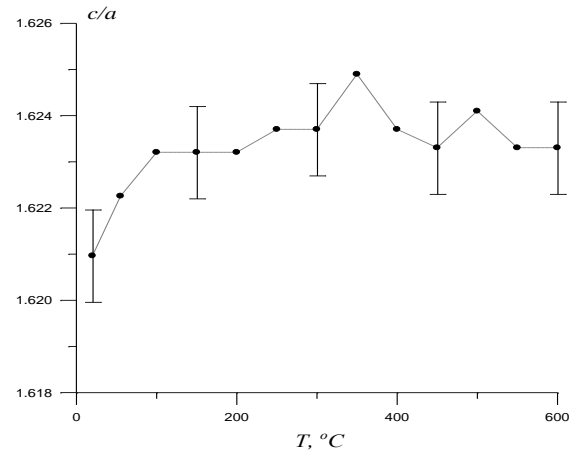
Fig. 5 – Dependence of the ratio c/a of NC cobalt on annealing temperature

4. CONCLUSIONS

According to electron microscopic studies in NC cobalt, obtained by SPD torsion, crystallite sizes do not exceed 25-50 nm. If the low-temperature annealing of NC cobalt to ~ 300 °C is accompanied by recovery, then annealing above 300 °C leads to the recrystallization of its structure. NC cobalt obtained by SPD torsion after heating above the phase transition temperature and cooling below this temperature retains the high-temperature fcc structure, which is prevented by the NC cobalt structure obtained by SPD. The delay mechanism of the fcc-hcp transition can be associated with changes in the size and strained state of crystallites. During plastic deformation, crystallite sizes decrease, and as a result, strong distortions arise in the volume of the crystal lattice, which can be caused by SPD dislocations and point defects [26].

In addition, during plastic deformation of cobalt hcp due to crystal lattice distortions, the packing density decreases as compared to the packing density of an ideal hcp structure, which leads to an increase in the elastic energy of the crystal. Due to the uniformity of the packing density and the proximity of the energy of the defect-free lattice of hcp and fcc cobalt, the energy of the hcp cobalt lattice subjected to SPD torsion may be higher than the energy of the fcc cobalt lattice, which may cause a delay of the fcc-hcp transition.

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Вплив інтенсивної пластичної деформації на фазові співвідношення нанокристалів кобальту

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Вибір кобальту як об'єкта дослідження пояснюється тим, що він характеризується низькою температурою поліморфного перетворення. Це дає можливість використовувати його як модельний матеріал для вивчення впливу розмірів кристалітів на характер цих переходів та фазовий склад. Наноструктуровані зразки кобальту були отримані методом інтенсивної пластичної деформації розтягування. Високий квазі-гідростатичний тиск у робочій зоні до 8 ГПа був створений на установці Бріджмана на ковадлі. Ковадлу виготовляли з карбіду вольфраму. Метод дозволяє отримати зразки високої чистоти без пор і домішок. Рентгенівські дифракційні дослідження проводилися на дифрактометрі DRON-7 з кобальтовим випромінюванням. Рентгенологічний аналіз проводили за методом Брегга-Брентано. Для проведення фазового аналізу використовували лінії Кα при кроці сканування 0,04 градуса, а при аналізі профілю дифракційних ліній та визначенні їх ширини – при 0,01 градуса. Абсолютна похибка вимірювання кутових положень дифракційних максимумів не перевищувала ± 0,020. Розмір нанокристалітів кобальту сягав близько 25-50 нм. Встановлено, що при низькотемпературному відпалі відбувається відновлення в структурі кобальту. Відпал вище 300 °C призводить до перекристалізації його структури. Нанокристалічний кобальт, отриманий при інтенсивній пластичній деформації розтягування після нагрівання вище температури фазового переходу та охолодження нижче цієї температури, зберігає високотемпературну структуру fcc. Показано, що характер затримки переходу fcc-hcp може бути пов'язаний зі зміною розміру та напруженого стану кристалітів, що утворюють нанокристалічний кобальт.

Ключові слова: Кобальт, Інтенсивна пластична деформація, Наноструктура, Метод Брегга-Брентано, Відпал, Відновлення, Рекристалізація, Структурні перетворення.