Structural studies of plastically deformed cobalt

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Abstract. This paper is devoted to the study of the fcc-hcp phase transition delay during cooling in nanocrystalline cobalt obtained by severe plastic deformation. Using the methods of X-ray and electron microscopy, it was revealed that this delay in the phase transition is due to the small size of the crystallites and the stressed state of the crystal lattice.

1. Introduction
Cobalt is one of the main components of alloys applied in magnetic recording devices. It is widely used as a catalyst for chemical reaction, as well as a material for thermoelectric devices. Due to the unusual physical properties, cobalt with ultrafine-grained and nanocrystalline (NC) structures presents great scientific and practical interest. It is known that NC cobalt can have both an hcp structure and a fcc structure. The physical properties of NC cobalt depend on the ratio of these phases. In turn, the ratio of fcc and hcp phases depends on the method of obtaining NC cobalt, the strain of deformation and the size of the crystallites, and a number of other factors. However, the results of research available in the literature are often contradictory [1-9]. We have already mentioned that the stability of fcc and hcp phases in NC cobalt in our opinion has not been sufficiently studied so far and requires more systematic research. This paper presents the results of studies of the structure and phase transformations in NC cobalt, obtained by severe plastic deformation (SPD) and subjected to subsequent annealing.

2. Experimental procedures and results
The NC samples were produced by SPD on Bridgman anvils under a pressure of ~ 7 GPa at room temperature by rotating the striker at 5 turns. Samples in different structural states were obtained by annealing at various temperatures. X-ray studies were carried out with a DRON-7 diffractometer on Co-radiation at room temperature. The microstructure was studied using a JEM-2000EX electron microscope.

According to the results of our electron microscopic studies, the microstructure of the samples after SPD is uniform, the grain boundaries are fuzzy and blurred. The average size of the crystallites is difficult to determine and it is about 20-50 nm. After annealing at 300 °C and 400 °C, partial recovery is observed in the samples, the grain boundaries remain blurred. After annealing at 500 °C, the primary recrystallization is completed and the grain sizes are approximately 200-500 nm. Electron microscope studies did not allow us to accurately determine the crystallite size. Therefore, to determine the phase composition in the samples and the crystallite size, we carried out X-ray studies. The diffractograms of SPD cobalt annealed at different temperatures are shown in figure 1. As can be seen from the figures, non-annealed SPD cobalt has an hcp structure at room temperature like non-
deformed coarse-grained cobalt. There are no clearly defined data on the stability of hcp and fcc phases of NC-cobalt. Thus, our results confirm that in NC-cobalt obtained by SPD, the hcp structure is preserved at room temperature. Samples annealed at temperatures up to 450 °C retain the hcp structure.

According to literature data for coarse-grained non-deformed cobalt, the temperature of the hcp-fcc phase transition lies in the interval from 387 °C to 440 °C. According to the point of view of a number of authors [7,9], the temperature of the hcp-fcc phase transition of cobalt decreases with decreasing the crystallite size. The results of our investigations did not reveal a noticeable decrease in the temperature of the fcc-hcp phase transition with a decrease in the size of crystallites to ~ 20 nm.

One can see from figure 1c that the samples annealed at 500 °C consist mainly of the high-temperature fcc phase. Samples annealed at temperatures from 600 °C to 900 °C consist of a mixture of the low-temperature hcp phase and the high-temperature fcc phase (figure 1d).

Figure 1. Diffractograms of SPD cobalt, annealed at different temperatures: a)-non-annealed sample; b)-T=450 °C; c)-T=500 °C; d)-T=900 °C.

Thus, according to the results of our research, the high-temperature fcc phase of NC-cobalt is retained after cooling to room temperature. We believe that the NC-structure of cobalt interferes with the transition of the high-temperature fcc phase to the low-temperature hcp phase upon cooling. We have already mentioned that this delay in the phase transition has not been studied sufficiently so far. We believe that the delay in the phase transition may be due to the small dimensions of the crystallites, the distortions and the stressed state of the crystal lattice. Since the distorted regions are the grain boundaries and the surface of the crystallites, the relative contribution of these regions to the elastic energy increases with decreasing the crystallite size. Therefore, for the fcc-hcp transition there must be
some critical size. The existence of a critical size of crystallites under which the martensitic transformation is blocked has also been discussed in the literature.

![Graph showing the dependence of the ratio of the hexagonal unit cell parameters c/a of the SPD cobalt on the annealing temperature](image)

**Figure 2.** Dependence of the ratio of the hexagonal unit cell parameters c/a of the SPD cobalt on the annealing temperature.

To confirm our assumptions about the stability of the hcp and fcc phases of NC cobalt, we investigated the dependence of the ratio of the hexagonal unit cell parameters c/a on the annealing temperature (figure 2). As can be seen from figure 2 for the non-annealed NC cobalt, the ratio is c/a = 1.621, that is noticeably smaller than this parameter for coarse-crystalline undeformed cobalt that equals to c/a = 1.632 and the theoretical value of this parameter is c/a = 1.633, which corresponds to the most stable state of the hcp structure. Consequently, the hcp phase of NC cobalt obtained by SPD is less stable than the hcp phase of coarse crystalline undeformed cobalt. When increasing the annealing temperature, the ratio of parameters c/a for NC cobalt increases to c/a = 1.6233. This indicates an increase in the stability of the hcp phase of NC cobalt with an increase in the annealing temperature.

To confirm our assumptions about the existence of the critical size for a fcc-hcp phase transition, we conducted studies of the coherent domain sizes (CDS) and the microstrains of the crystalline lattice as a function of the annealing temperature. The CDS and microstrain were determined by measuring the broadening of diffraction lines. The CDS were calculated with the help of the Scherrer formula using lines located at small diffraction angles:

$$D = \frac{\lambda}{W \cos \theta}$$  \hspace{1cm} (1)

Here \(\lambda\) is the wavelength of the X-ray radiation; \(W\) is the physical broadening of the diffraction line; \(\theta\) is the diffraction angle. The values of the microstrain \(<\varepsilon^2>^{1/2} = \Delta a/a\) were determined by the diffraction lines at large angles according to the formula:

$$W = 4 <\varepsilon^2>^{1/2} \tan \theta$$  \hspace{1cm} (2)

Here \(a\) is the average unit cell parameter and \(\Delta a\) is the average unit cell parameter deviation from the \(a\) value. Microstrains were also determined taking into account the contribution of CDS to the broadening of X-ray lines by the formula:

$$<\varepsilon^2>^{1/2} = \left( W - \frac{\lambda}{D \cos \theta} \right) \left( \tan \theta \right)^{-1}$$  \hspace{1cm} (3)

In addition, the average CDS and the microstrains \(<\varepsilon^2>^{1/2}\) were determined from the Williamson-Hall relations

$$W \times \cos \theta = \frac{\lambda}{D} + 4 <\varepsilon^2>^{1/2} \sin \theta.$$  \hspace{1cm} (4)

Figure 3 shows that the CDS, determined by the Scherrer formula and the Williamson-Hall curves, are close. The values of D up to the annealing temperature T~300 °C vary insignificantly in the interval from ~250 Å to ~500 Å. These results agree well with our electron microscopic data. At annealing temperatures above 450 °C, a sharp increase in the CDS is observed. Thus, the obtained
results confirm our assumptions that the delay of the fcc-hcp phase transition in SPD cobalt is related to the smallness of the CDS. At annealing temperatures above 500 °C, some crystallites of the fcc phase grow to a critical size and, upon cooling, pass to the hcp phase. According to our results, the critical size for the fcc-hcp transition is approximately \( D \sim 1000 \, \text{Å} \).

**Figure 3.** Dependence of the coherent domain sizes on the annealing temperature, determined: 1 - by the Scherrer formula, 2 - from the Williamson-Hall curves.

**Figure 4.** Dependence of the microstrains in SPD cobalt on the annealing temperature, determined: 1 - by formula 2; 2 - by formula 3; 3 - from the Williamson-Hall curves.

In the calculations of \( \langle \varepsilon^2 \rangle^{1/2} \), using formula (3), the values of \( D \) determined from the line (100) were used, and their dependence on the annealing temperature was taken into account. As can be seen from figure 4, the values of microstrains determined by various methods differ only for annealing temperatures below 300 °C for the recovery region. Microstrains decrease with an increase in the annealing temperature and at annealing temperatures above 400 °C take a value equal to \( \sim 2 \times 10^{-4} \). This temperature is close to the temperature of a sharp increase in the CDS. This makes it possible to assume that the reasons for the delay of the fcc-hcp phase transition in SPD cobalt are the small dimensions of the crystallites and the strained state of the crystal lattice.

3. Conclusions

Thus, we have shown that the delay of the fcc-hcp phase transition in NC cobalt, obtained by SPD is due to the small crystallite size and the strained state of the crystal lattice.

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