Phase transitions Co−C nanocomposite at heating

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Differential scanning calorimetry was used to study the Co−C nanocomposite, which is an array of ultrathin carbon nanocages encapsulated cobalt nanoparticles. The activation energy of the $\alpha \to \beta$ transformation of the nanocomposite and the value of its endothermic effect have been estimated. Thermal effect is much greater than those values that correspond to the observation conditions for $\alpha \to \beta$ transformations in massive cobalt samples. The idea was put forward that transitional transformation is assumed by a non-diffusion, massive mechanism.

Keywords: phase transitions, carbon nanocages, cobalt, activation energy.

Nanocomposites, which are a 3D network of carbon nanocells containing paramagnetic or ferromagnetic clusters of nanoparticles 3−5 nm in size, have special physical properties due to the size effect and geometry of the material [1]. The special properties of these nanocomposites include high specific surface area, high electrical conductivity, superparamagnetism, chemical and mechanical stability [2,3]. Therefore, at present, such materials have wide prospects for application in the field of photonics, electrochemistry, and catalysis for renewable energy sources [3–6], and are also of interest in polymorphic transformations. As it is known, Co and Fe exhibit polymorphism, but we have not found any information on the effect of this specific state on allotropic transformations (first-order phase transition) in such materials. Besides, isolation from the external environment by carbon makes it possible to avoid undesirable chemical reactions in a metal nanoparticle.

In this paper, we present the results of study by a precision differential scanning calorimetry (DSC) [7] of Co−C nanocomposites in comparison with bulk cobalt (mCo). The aim of this paper is to study the behavior of thermal effects during heating of the Co−C nanocomposite.

The materials under study were obtained by pyrolysis at a temperature of 600°C in a nitrogen atmosphere [8]. The thermal properties of the samples under study were determined using device STA Jupiter 449 (Netzsch Holding). Heating was carried out in an argon atmosphere at a rate of 5−40 K/min. The gas flow rate was 25−30 ml/min. The experimental DSC data were processed using software „Proteus Analyses"and „Fityk".

A study of the nanocomposite structure showed that it is similar in shape to a rod of inclusions of close-packed and closely interacting cobalt (nCo) nanoparticles coated with a multilayer graphite network [8]. Carbon prevents the agglomeration of nanoparticles in such mixture, which is a black dispersed powder. The size of nCo nanoparticles is in the range of 3−5 nm. This powder, due to nCo presence in it, has ferromagnetic properties.

Fig. 1, a shows the change in the DSC signal and its second derivative with respect to temperature (DDDSC) upon heating the test sample. The DSC dependence exhibits several endothermic features. The course of DDDSC shows that the features of DSC signal change are localized in a rather narrow temperature range from 380 to 480°C. According to [9], such a combination of extrema in the DSC- and DDDSC- dependences indicate the development of a first-order phase transformation in this temperature range. As applied to the nCo−C nanocomposite, this is the temperature range of the polymorphic ($\alpha \to \beta$, hcp→fcc) transformation in cobalt from the low-temperature to the high-temperature phase.

Fig. 2, a shows data on the change in the DSC signal upon heating at different rates nCo−C. A pronounced endothermic effect is observed, which shifts to higher temperatures region with the heating rate increasing. The thermal effect of transformation (Q) for the first heating at a rate of 5°C/min is approximately 18 J/g, and as the heating rate increases, it tends to decrease to 10 J/g. These values are noticeably larger than the values (5.3 and 3.4 J/g, respectively) that are observed for mCo [10].

Upon repeated heating of the samples under study (Fig. 1, b and 2, b), the patterns noted above for the DSC signal are preserved. However, the type of the DDDSC signal in the region of $\alpha \to \beta$-transformation development temperature indicates a more complex nature of the development of phase recrystallization in this temperature range during nCo−C heating. In this case, the magnitude of the thermal effect sharply increases, which increases noticeably with the heating rate increasing: $Q = 45 \to 65$ J/g.

Since nCo particles are in a carbon medium with the possible presence of a CO compound and adsorbed oxygen, when the nanocomposite under study is heated the chemical interaction of nCo with these components is possible.
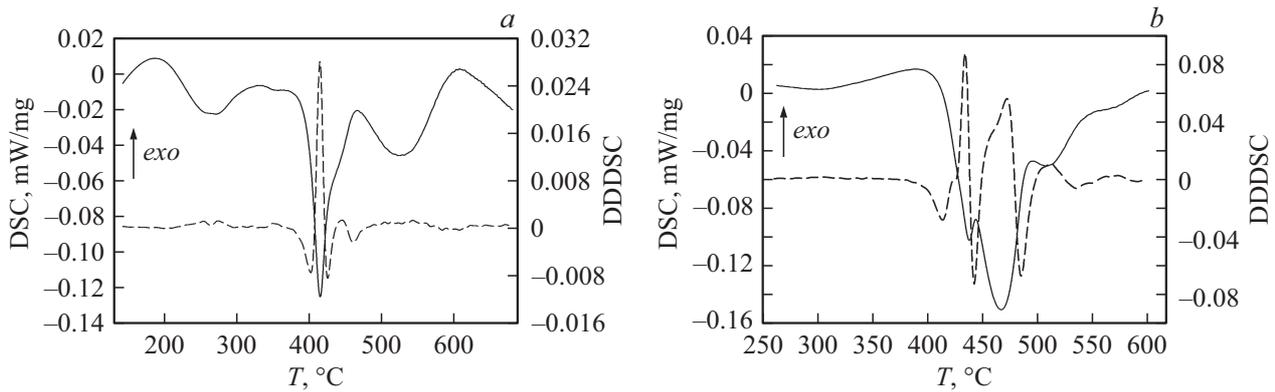
Figure 1. Change in the DSC (solid line) and DDDSC (dashed line) signals during heating of *n*Co−C nanocomposite at a rate of 10°C/min. First (*a*) and second (*b*) heatings.
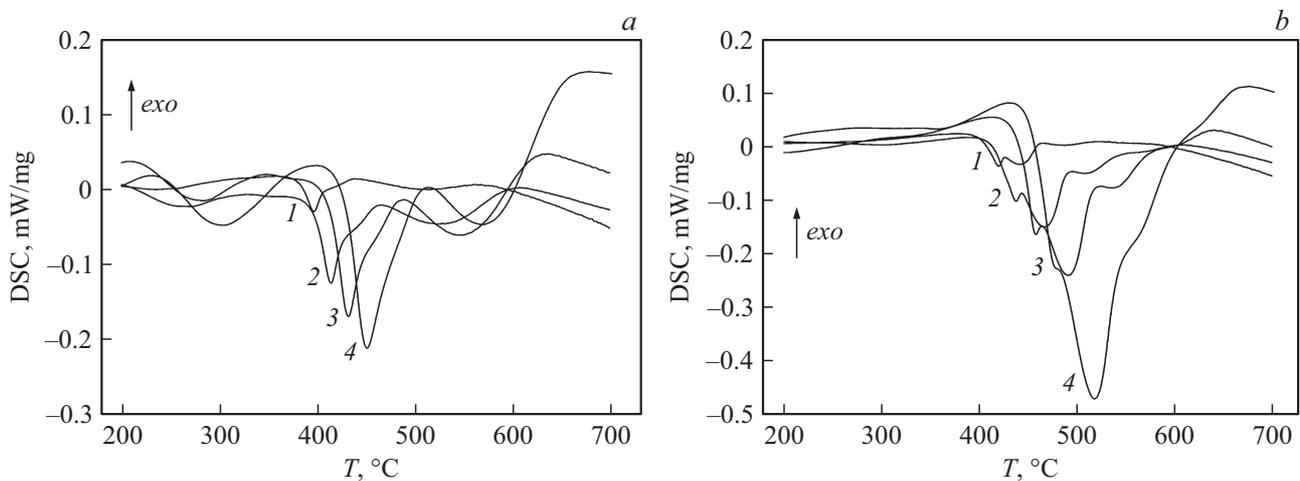
Figure 2. Influence of the *n*Co−C nanocomposite heating rate on the type and arrangement of endothermic peaks: 5 (*1*), 10 (*2*), 20 (*3*) and 40°C/min (*4*). First (*a*) and second (*b*) heatings.

The reaction of Co interaction with oxygen should proceed at temperatures of about 500°C [11] and be accompanied by heat release. This is higher than the temperature of registration of endothermic effects on the obtained DSC dependences. The reaction between cobalt and carbon monoxide (CO) with the formation of cobalt carbide and carbon monoxide proceeds at temperatures up to 220°C. This reaction is also exothermic, and its direct implementation is difficult [11]. In direct contact, the interaction of Co with carbon does not occur under normal conditions and is carried out in more complex chemical reactions [11]. Therefore, there are every reasons to believe that the possible chemical reactions of Co with the listed components do not make a significant contribution to the endothermic effect during the $\alpha \rightarrow \beta$ transformation into *n*Co.

Besides, the expected products of the interaction of cobalt nanoparticles with carbon dioxide, carbon, or oxygen are paramagnetic, while after heating the nanocomposite to 1200°C, its ferrimagnetic properties are retained. Registered in nanocomposites and the Curie point. The data on

re-heating (Fig. 1, *b* and 2, *b*) demonstrate the preservation of the previously noted patterns of change in the DSC signal during the $\alpha \rightarrow \beta$-transformation into *n*Co and are also characterized by the presence of the Curie point.

Estimation by the Kissinger method [12] of the activation energy of the phase transformation $\alpha \rightarrow \beta$ into *n*Co−C for the first and second heatings gave close values: 140 ± 10 kJ/mol.

As can be seen from Fig. 1, *b* and 2, *b*, the course of the DSC-curve in the region of registration of the endothermic effect indicates that phase recrystallization is a superposition of several components, which is especially well seen from Fig. 3. Indeed, analysis of the data (Fig. 3) on endothermic maxima during the first and second heatings shows that these effects are superpositions of several components implemented in close temperature ranges. This complication of the process of phase recrystallization is clearly manifested when the samples under study are reheated.

Comparison with the data obtained for the *m*Co samples [10] allows us to make the following generalizations.
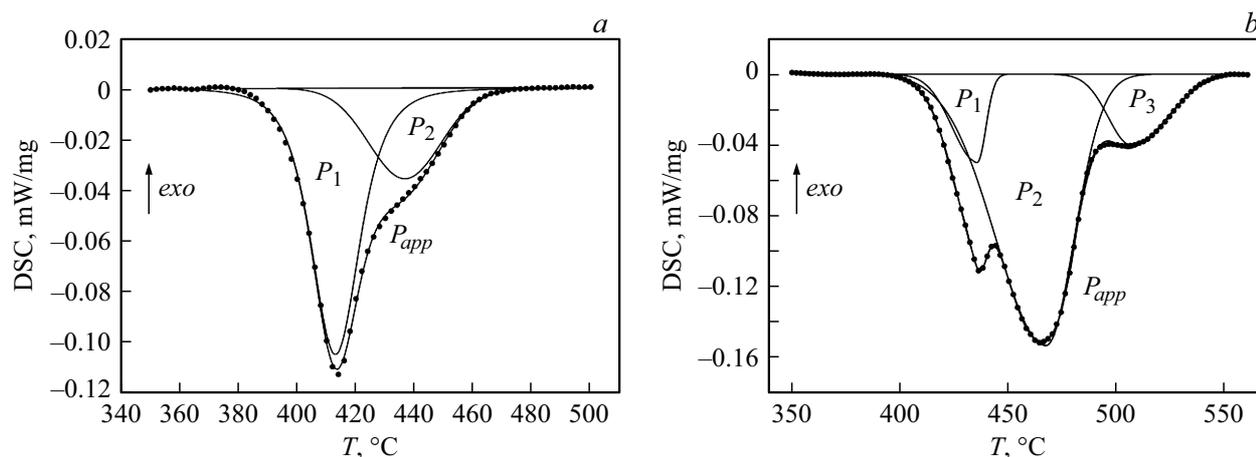
Figure 3. Structure of endothermic peaks during heating of the nCo−C nanocomposite at rate of $10°$C/min. First (a) and second (b) heatings. Points represent experimental data; P_{app} is the result of approximation; P_1, P_2, P_3 — subpeaks.

1. Polymorphic transformation during nCo−C heating occurs at lower temperatures than in mCo.

2. The thermal effect of the transformation into nCo−C is by several times greater than the values during the phase transformation into mCo.

3. The activation energy of phase transformations during heating in nCo−C does not depend on heating cycles. In this case, it is significantly less than the values determined under similar conditions for mCo ($230-370$ kJ/mol).

4. nCo−C reheating is characterized by transformation temperature shift towards higher temperatures compared to the initial heating and is accompanied by increase in the thermal effect of transformation.

Taking into account the very small size of nCo particles and the relatively low phase transformation temperature and activation energy, it can be assumed that this transition occurs by a diffusionless massive mechanism.

The presence of two maxima in the spectrum of the endothermic effect may be due to the presence in the structure of predominantly two groups of nCo−C particles differing in size. Reheating leads to even greater differentiation of such particles in size. With the heating rate increasing, the differences in the DSC dependences due to the size of particles nCo−C decrease (Fig. 2, b).

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Conflict of interest

The authors declare that they have no conflict of interest.

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