

Thermally Stimulated Transformation of Micellar Tungsten Glycolate into Nanodisperse Tungsten Carbide

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The increasingly strict requirements for the quality and performance of metalworking tools stimulate the development of new methods for synthesizing nanodisperse WC powders and hard alloys on their basis [1]. Among these methods are high-energy grinding [2], spray conversion of homogeneous solutions of a precursor [1, 3], and various gas-phase [4] and plasma-chemical [1, 5] synthesis methods. The recrystallization of the synthesis products is suppressed by various variants of hot isostatic and electric-pulse pressing and high-frequency induction heating [1, 6]. For the same purpose, WC grain growth inhibitors, such as vanadium and chromium carbides and Group IV and V metal carbonitrides, are introduced into the initial WC–Co hard-alloy mixtures [7]. To this effect, the usual fine WC–Co reaction mixture is also diluted by nanoparticles of the carbide phase. Note, however, that addition of WC nanoparticles to the initial mixture, i.e., transition to a bimodal size distribution of WC grains, typically gives rise to various inhomogeneities in a sintered composite and favors the development of pore and crack formation processes [1].

In comparison with the above methods, colloid-chemical techniques for synthesizing precursors for producing nanodisperse WC–Co composites have a number of technological advantages. On the one hand, these are the guarantee of mixing of the initial components of a hard alloy at the molecular level, the possibility of controlling the dispersity of precursor particles, and a considerable decrease in power consumption and synthesis time [8]. On the other hand, the known tendency of nanoparticles to aggregate [9] and form of a certain hierarchy in the size distribution

of aggregates of particles [10] allows one to replace spontaneous aggregation by controlled structuring and self-assembly of molecular fragments of the precursor in solution to produce liquid-crystal structures [11].

In this work, we solved the problem of using the phenomena of the formation and structuring of micelles for imparting certain size and structure to WC precursor particles at the WC synthesis stage with subsequent production of submicron and nanodisperse particles of WC powders and WC–Co mixtures. Particular attention was paid to testing the hypothesis that the supramolecular structure of a precursor is inherited by the product of its thermal decomposition–reduction.

EXPERIMENTAL

A WC precursor (W-EG) was synthesized by the interaction of tungsten glycolate, ethylene glycol, and carbon black [12], and a WC–Co precursor (WCo-EG) was produced by the interaction of ammonium tungstate, a cobalt salt, ethylene glycol, and citric acid [13]. Next, both precursors were subjected to heat treatment in a SShVL vacuum furnace within the temperature range 600–1400°C for 10–60 min, and the decomposition (carbideization) products were then cooled at a rate of 200 K/min. The physicochemical characteristics of the synthesized samples were determined by chemical analysis, X-ray diffraction analysis with a MAXima-X XRD-7000 X-ray diffractometer (Shimadzu, Japan), electron microscopy, energy dispersive X-ray analysis for local elemental identification with a JSM-6390LA scanning electron microscope with a JED-2300T energy dispersive X-ray analyzer (JEOL, Japan), and scanning tunneling microscopy with an SMM 2000 tunneling microscope. The fractal dimensions of the length (section

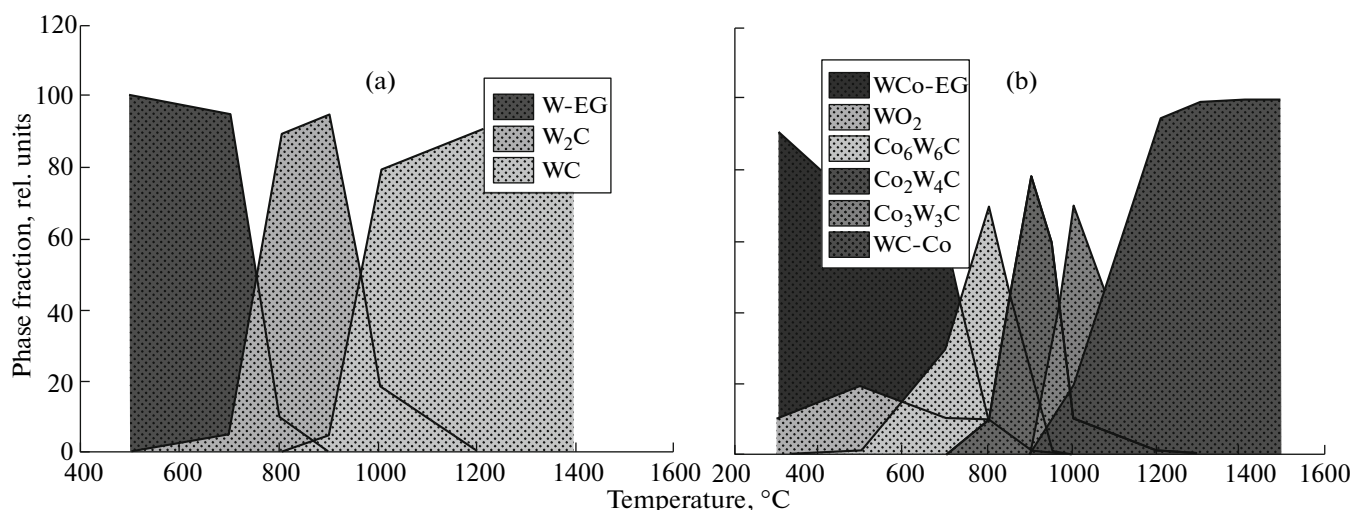
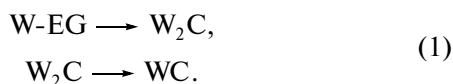


Fig. 1. Temperature dependence of phase transformations (a) by reactions (1) with the precursor W-EG and (b) by reactions (2) with the precursor WCo-EG.

FD) and area (area FD) of the analysis objects were found using a program for the SMM 2000 tunneling microscope.

RESULTS AND DISCUSSION

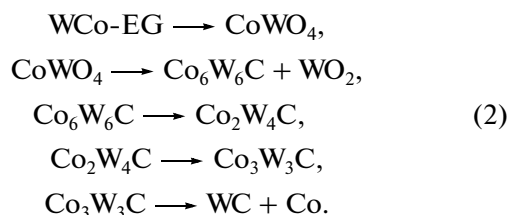
X-ray diffraction analysis showed that both precursors were X-ray amorphous substances and their compositions were 27.7 wt % C, 26.1 wt % O, 46.1 wt % W, and 1.0 wt % H for W-EG and 20.0 wt % C, 18.3 wt % O, 46.7 wt % W, 15.0 wt % Co, and 1.2 wt % H for W-EG. It was found (Fig. 1) that the sequence of phase transformations in the decomposition–reduction of each precursor to the desired product depends on its composition. For example, the synthesis of the carbide WC from the precursor W-EG is accompanied by an increase in temperature from 600 to 700°C and occurs through an intermediate stage of formation of the lower carbide W_2C :



Since the fractal dimensions of the length and area of particles during transformation (1) remain unchanged (Fig. 2), it can be concluded that the change in the chemical and phase compositions of the precursor W-EG is not accompanied by a change in the morphology of the forming carbide particles. Only at treatment temperatures of 800°C and higher, their average size D abruptly increases, which agrees with published data [1–3].

Addition of a cobalt salt to the precursor in the mole ratio W:Co = 1:1 increases the number of stages of its transformation into the end product. The X-ray diffraction data and their based phase transformation diagram (Fig. 3) suggested that the process

within the temperature range 800–1000°C occurs as the following sequence of transformations:



As in the pure tungsten carbide synthesis, in the course of sequence of transformations (2), the morphology of the initial substance is conserved, which is indicated by the constancy of the fractal dimensions of the length and area of particles of the precursor and its decomposition–reduction products. At the same

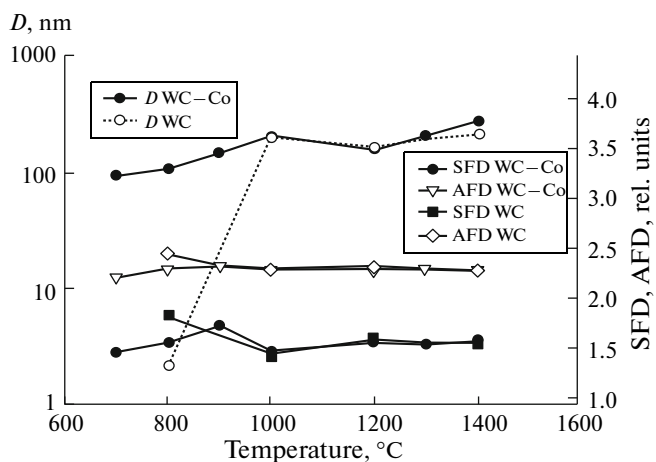


Fig. 2. Changes in the particle size D and their fractal dimensions SFD and AFD of the length and area, respectively, in the syntheses of the carbide WC by reactions (1) and the WC–Co mixture by reactions (2).

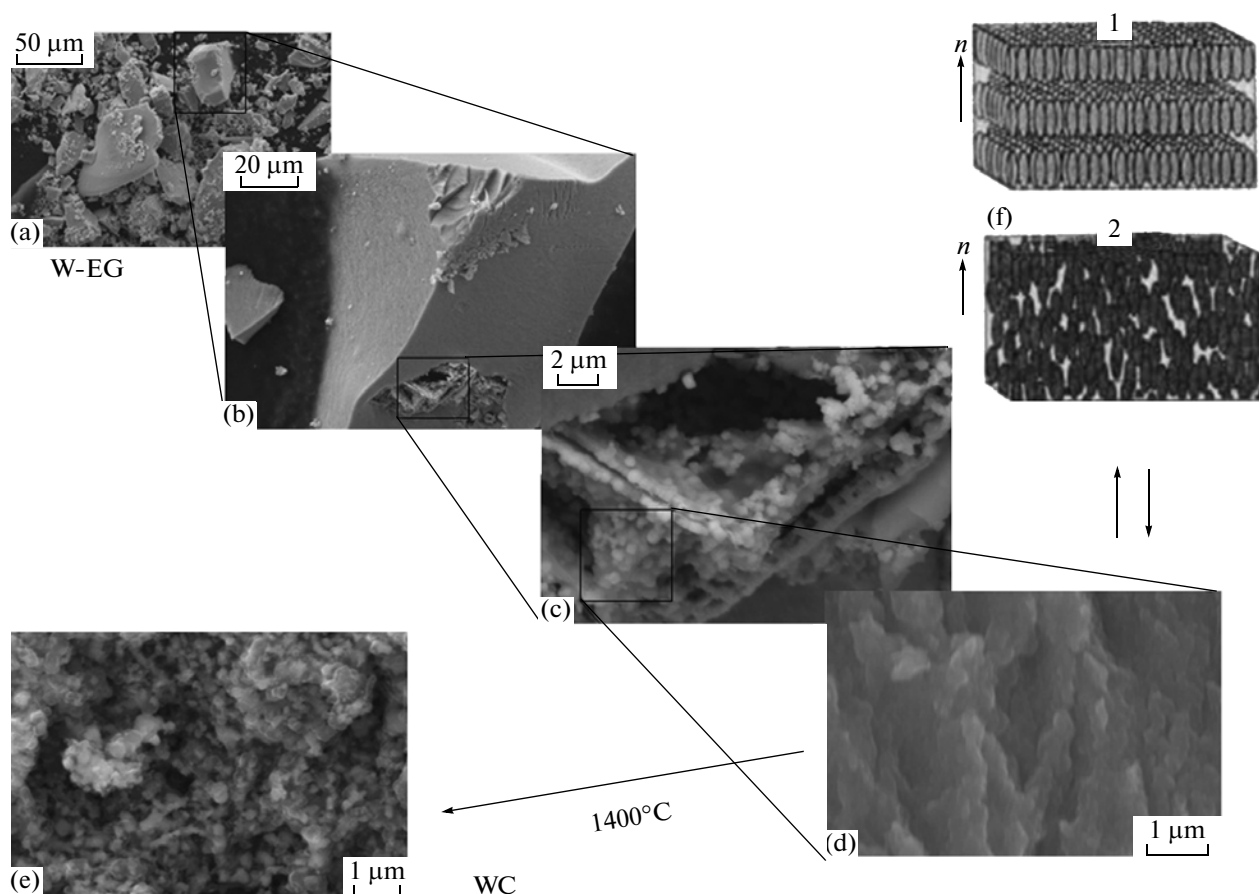


Fig. 3. Evolution of the structure of the precursor W-EG in vacuum heat treatment: (a–d) precursor structures, (e) structure of single-phase WC produced by reactions (2) in 10 min, and structures of (f1) smectic and (f2) nematic liquid crystals. n is the ordering direction vector [14].

time, the temperature dependences of the rates of growth of particles of the end product for the precursors differ at low temperatures but become virtually identical at temperatures above 850–900°C (Fig. 2).

The reasons why tungsten carbide inherits the structure from the precursor can be understood by comparing the particle morphologies determined by electron microscopy. Figure 3 shows that the precursor precipitating from the ethylene glycol reaction solution forms pseudocrystals consisting of chains of spherical tungsten-containing particles ordered in one direction, which are similar in texture to nematic liquid crystals (Figs. 3f1 and 3f2). The same morphology is conserved in the product of carbothermic synthesis (tungsten carbide WC) below the temperature of the onset of its recrystallization (Fig. 3e). The formation of pseudocrystals of the carbide phase from the precursor in a colloidal solution as early as the initial synthesis stages allows one to control the aggregation of micelles (e.g., by introducing surfactants or changing the solution viscosity or temperature) and, hence, the size of primarily forming particles and the way of their ordering [14].

Thus, by the example of the synthesis of the carbide WC and the WC–Co hard-alloy mixture, we have shown that, if a carbide precursor is colloidal pseudocrystals consisting of nanodisperse particles, then, regardless of the number of stages of carbothermic reduction of the precursor, its pseudocrystalline structure and the particle size remain virtually unchanged in the course of transformation of the precursor into the end product. The short (~10 min within the temperature range 800–1400°C) time of the transformation of the precursor into the end-product phase is indicative of a kinetically controlled mode of the process, which, in its turn, opens the way to producing nano- and ultradisperse high-temperature carbide phases with a given size hierarchy.

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