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Fine Tungsten from W/MgO Mechanocomposite Obtained by the Reduction of Tungsten (VI) Oxide by Magnesium

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Abstract

The effect of stoichiometric compositions and the conditions of mechanical activation on the formation of the product of WO_3 reduction by magnesium was studied by means of X-ray phase analysis. In the process of mechanical activation of a mixture of tungsten (VI) oxide with magnesium at the corresponding stages, mechanochemical composites of various compositions are formed, including magnesium, tungsten (VI and IV) oxides, magnesium tungstate, tungsten and magnesium oxide. The reduction of tungsten (VI) oxide with magnesium is completed by 8 min of activation with the formation of a W/MgO composite. The conditions for the acid separation of tungsten from magnesium oxide from mechanochemical composites W/MgO were determined. It was shown with the help of scanning electron microscopy that tungsten separated from magnesium oxide is highly dispersed and consists of primary particles that are close to spherical in shape, with sizes from 50 to 100 nm, aggregated into secondary particles from 1 to 10 microns in size. Magnesium content in finely dispersed tungsten powder, determined by means of energy dispersive analysis, is less than 2 mass %.

Keywords: mechanochemical reduction, fine tungsten, high-energy systems

INTRODUCTION

The technology of manufacture of products based on tungsten and its alloys possessing high heat resistance, infusibility, chemical stability, corrosion resistance is directly connected with powder metallurgy. Fine tungsten powders find application in the production of electric contacts, composites with copper, nickel and other metals, pyrotechnic products with directed action, and as fillers in compounds for piesoelectric transformers, polymer modifying agents, catalysts, sintered semi-products and other products.

As a rule, fine tungsten powders are obtained by means of reduction by hydrogen [1] and metallothermic reduction of its compounds both in the mode of self-propagating high-temperature synthesis (SHS) [2] and it salt melts [3].

The results presented in the present paper continue the studies of the mechanochemical reduction of metal oxides by active metals with the formation of $M/(Me_{act})_xO_y)$ composites – powder mixtures of the fine particles of reduced metals and an oxide of an active metal for the purpose of recovery of fine metals from the composite by acid-based separation from the oxide of an active metal [4, 5]. In comparison with other methods of obtaining fine powder materials, mechanochemical synthesis (MCS) is distinguished by the short reaction time and simultaneous elimination of a number of problems connected with environmental pollution. The reduction of metal oxides having E^0_{298} $(M^{n+}/M) > 0$ V by active metals with E^0_{298} $(Me^{n+}_{act}/Me_{act}) < -0.7$ V proceeding with the high exothermal effect may be realized during a single stage of mechanical activation (MA) [6–8], which promotes an increase in the contact surface area, acceleration of mass transfer and therefore activation of the mechanochemical interaction with the formation of fine composites ($M/(Me_{act})_xO_y$).

The extraction of reduced metal from this composite without distortion of its fine dispersed state is determined by the choice of a solvent for the oxide of the active metal. This solvent should be inert with respect to the reduced metal. Among active metals, magnesium is used most efficiently because the phase of magnesium oxide is formed during the mechanochemical reduction-oxidation reaction, which is highly exothermal as a rule. This magnesium oxide phase prevents substantial agglomeration of the products of mechanical activation. Magnesium oxide forms readily soluble compounds in the interaction with the aqueous solutions of HCl or H_2SO_4 [9]. In the solutions of hydrochloric acid in the presence of oxygen, tungsten may be oxidized to W^{5+} with the corresponding blue colour of the solutions [10]. In the diluted solutions of sulphuric acid at 298 K, tungsten does not get dissolved, and it may be separated from the W/MgO composite without any distortion of the finely dispersed state. The application of metal oxide reduction by magnesium by means of mechanical activation for the synthesis of M/MgO catalysts is known [11, 12].

The goal of the present paper was to study mechanochemical interaction in the system of tungsten (VI) with magnesium, to determine the conditions for the formation of W/MgO composites and for the recovery of fine tungsten from them.

EXPERIMENTAL

The reagents used in the work were WO_3 (TU 6-09-397–75), magnesium powder (GOST 6001–79, MPF-2); sulphuric acid (GOST 14262–78), acetone (GOST 14262-78).

The mixtures of magnesium and tungsten oxide with different stoichiometric compositions were treated in a high-energy ball planetary mill AGO-2 (cylinder volume 250 cm^3, ball diameter 5 mm, the mass of ball load 200 g, sample portion 10 g, the frequency of cylinder rotation around a common axis 600 and 1000 r.p.m.).

Investigations by means of X-ray phase analysis (XPA) were carried out with the help of a D8 Advance diffractometer (Bruker, Germany) with the characteristic radiation $CuK_{\alpha 1}$ (λ = 1.5406 Å). The phase composition was determined using the PDF-2 database.

Investigation of the morphology of the resulting samples was carried out using scanning electron microscopes (SEM) OXFORD INSTRUMENTS (England) and Hitachi TM 1000 (Japan). The microscope Hitachi TM 1000 was equipped with a TM 1000 EDS detector intended for the determination of the chemical composition of the sample.

RESULTS AND DISCUSSION

The reduction of tungsten (VI) oxide by magnesium is an exothermal process with the evolution of a large amount of heat:

$$WO_3 + 3Mg \rightarrow 3MgO + W; \ \Delta_r H^0_{298} \approx -963 \text{ kJ} \qquad (1)$$

It was shown in the thermal analysis studies of WO_3 reduction by magnesium [13] that the interaction between the components starts before the melting point of magnesium (T_m = 924 K), proceeds with a high rate, is accompanied by a powerful exothermal effect starting at 873 K. An intense exothermal effect observed at the differential curve at 873–973 K, which is connected with the chemical interaction between tungsten oxide and magnesium, is the evidence of the high reactivity of magnesium with respect to tungsten oxide. During the mechanical activation of a mixture of tungsten (VI) oxide with magnesium, another exothermal reaction with the formation of magnesium tungstate is possible:

$$WO_3 + MgO \rightarrow MgWO_4; \ \Delta_r H^0_{298} \approx -74 \text{ kJ} \qquad (2)$$

It was demonstrated in [14] that magnesium tungstate $MgWO_4$ may be synthesized within three cycles of sintering – grinding at 1273 K. Thermal effects of reactions (1) and (2) are given with the account of the standard enthalpies of formation for WO_3, MgO and $MgWO_4$ [15].

During MA, the formation of the composites differing from each other in composition takes place. These composites involve tungsten, magnesium oxide, tungsten (IV) oxide, magnesium, magnesium tungstate ($MgWO_4$), Fe (from the mill material), which was controlled by means of XPA (PDF-2). Preliminary studies by means of XPA showed that the mechanochemical reduction of tungsten oxide by magnesium within activation time less than 30 min is achieved only with the frequency of cylinder rotation around the common axis 1000 r.p.m. and the stoichiometric ratio of the components in the system WO_3 / Mg = 1 : 3.6.

Investigation of the effect of MA time (τ_a) from 0.5 to 8 min for a mixture of WO_3 + Mg under the above-indicated conditions (Fig. 1) on

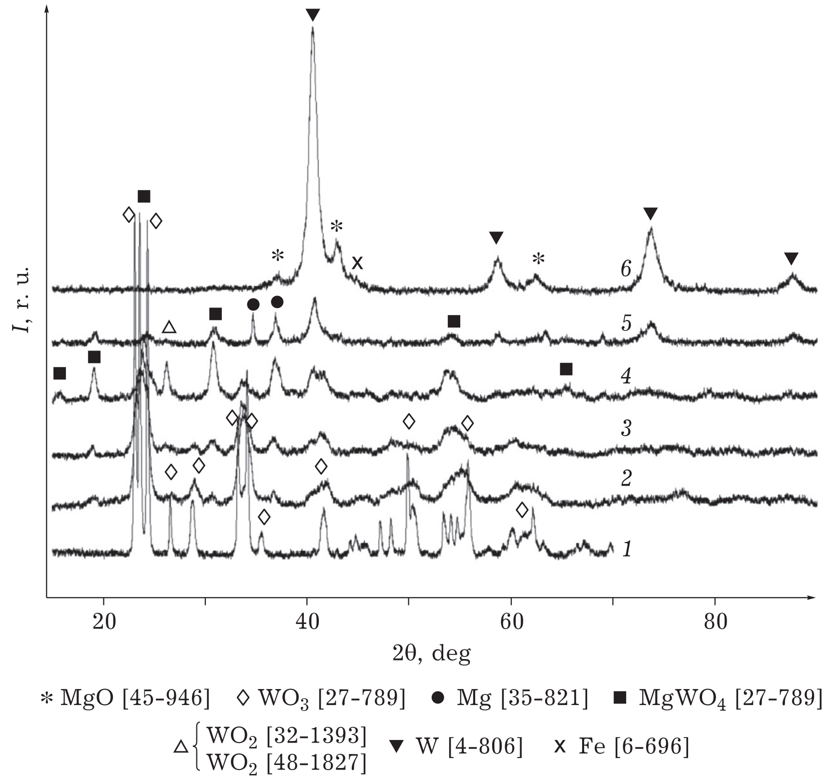

Fig. 1. Diffraction patterns of samples: WO_3 before MA (*1*) and mechanocomposites of different compositions at τ_a = 0.5 (*2*), 1 (*3*), 2 (*4*), 4 (*5*), 8 (*6*) min in the atmosphere of Ar.

the degree of the reduction of tungsten oxide by magnesium showed that within τ_a = 0.5 min the intensities of reflections from WO_3 and Mg in the diffraction patterns of the samples decrease (see Fig. 1, curve *2*). An increase in τ_a to 1 and 2 min leads to a further decrease in the intensity of reflections from WO_3, Mg; the reflections from MgO and W are not observed but the reflections corresponding to the $MgWO_4$ phase appear. With an increase in τ_a to 2 min (see Fig. 1, curves *3*, *4*), their intensities increase. At τ_a = 4 min, the reflections from W and MgO appear in the diffraction patterns; their intensities are low. At the same time, the intensity of reflections from $MgWO_4$ decreases (see Fig. 1, curve *5*). An increase in activation time to 8 min leads to the formation of W/MgO mechanocomposite: only broadened reflections from W and MgO are recorded in the diffraction patterns, while reflections from other phases are absent (see Fig. 1, curve *6*). The possibility of the metallothermal reduction of magnesium tungstate in the exothermal reaction with the release of a large amount of heat was demonstrated in [13, 14]:

$$MgWO_4 + 3Mg \rightarrow W + 4MgO;$$
$$\Delta_r H^0_{298} \approx -874.8 \text{ kJ} \qquad (3)$$

It is likely that the mechanochemical reduction of tungsten (VI) oxide by magnesium proceeds also through the formation of magnesium tungstate, and with an increase in activation time it proceeds to subsequent reduction of $MgWO_4$ by magnesium.

Investigation of the resulting W/MgO composite samples by means of scanning electron microscopy showed that the primary particles of mechanochemical composites formed during τ_a = 8 min have a shape close to spherical, 50-100 nm in size, and are aggregated in larger particles 1–20 μm in size (see Fig. 2, 3). The stability of W/MgO composites during storage under usual conditions for several months was confirmed by the results of XPA.

The W/MgO composites obtained by means of MA for 8 min with the stoichiometric component ratio WO_3 / Mg = 1 : 3.6 and the frequency of cylinder rotation around the common axis 1000 r.p.m. were studied with respect to the isolation of tungsten from the side products of reduction (Fig. 3), such as magnesium oxide and tungsten oxides. Magnesium oxide is most efficiently dissolved in the solutions of HCl and H_2SO_4 [9]. To separate tungsten particles from magnesium oxide, we studied the treatment of W/MgO mechano-

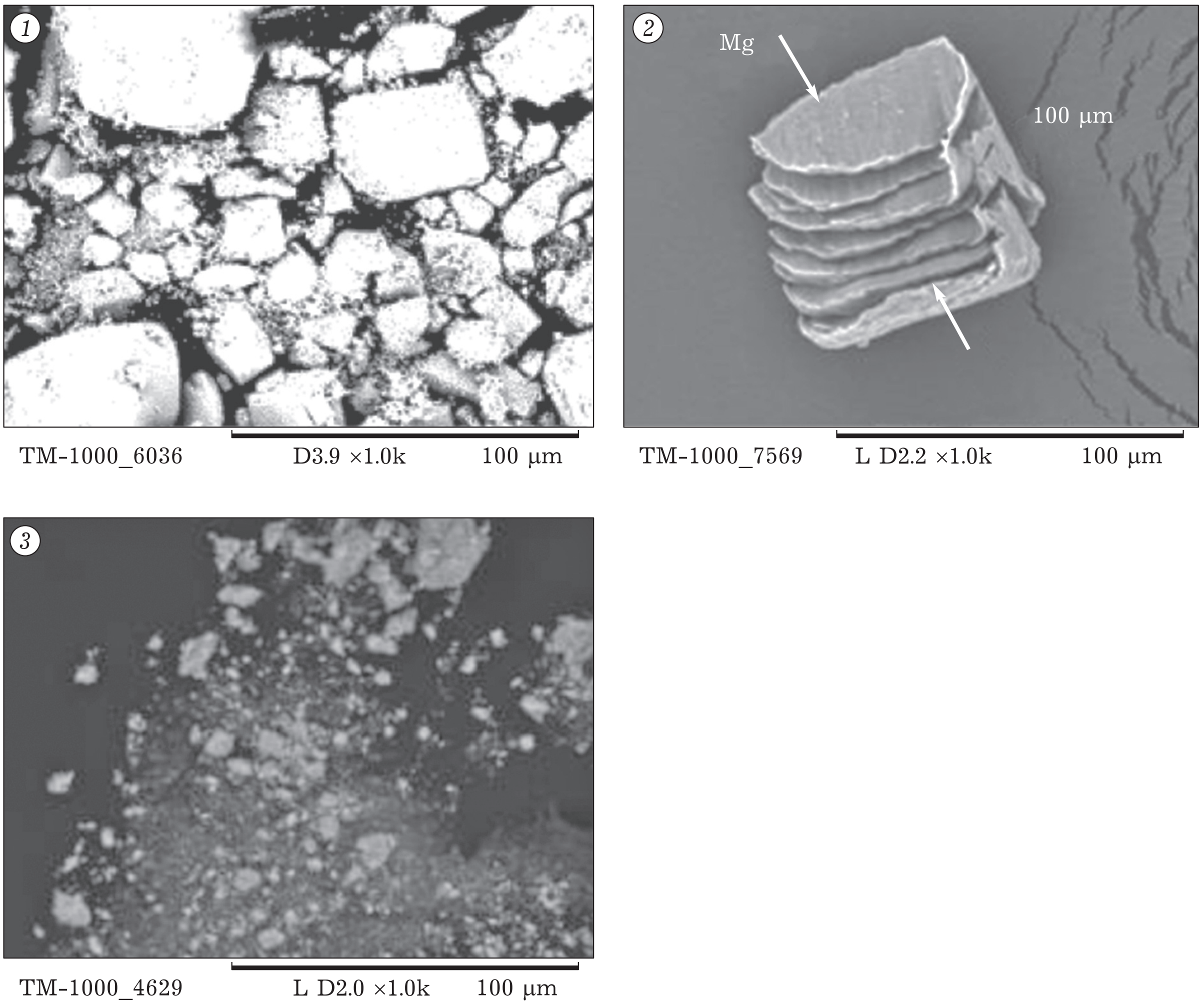

Fig. 2. Electron microphotographs of WO_3 (*1*), Mg (*2*) and W/MgO mechanocomposite activated for 8 min in the atmosphere of Ar (*3*). Card Nos. from the PDF-2 database for the compounds are given.

chemical composites with the diluted solutions of these acids. A comparison of the results of the treatment of W/MgO with the diluted acid solutions revealed the advantage of the use of H_2SO_4 because a blue or light blue colour appeared in the solutions of HCl, which may be connected with the possibility of partial oxidation of fine tungsten to W^{5+} [10].

The optimal conditions for tungsten separation from the most abundant side product (magnesium oxide) in the composite were determined: treatment with a 1 M H_2SO_4 solution (298 K; 30 min) and with distilled water. Tungsten remains in the form of powder.

After treatment with sulphuric acid, mechanochemical composites W/MgO could still contain residual amounts of tungsten oxides, so additional treatment of the composites with a 4 % solution of hydrofluoric acid was carried out.

It was revealed by means of XPA that the oxidation of tungsten powder starts at the stage of removal of the residual amount of water (during drying in the air at ~343 K) (see Fig. 3, curve *4*). To eliminate the electrochemical corrosion of tungsten, moisture was removed from the surface of its particles by washing with acetone. Only tungsten reflections are present in the diffraction patterns of the samples obtained by sequential treatment of W/MgO composites with a 1 M H_2SO_4 solution, water, 4 % solution of HF, water and acetone.

Determination of the size of tungsten powder particles after separation from side components from the W/MgO mechanocomposite was carried out by means of scanning electron microscopy. It was shown that the particles of fine tungsten powder are secondary aggregates 1–10 µm in size, composed of primary particles 50–100 nm in

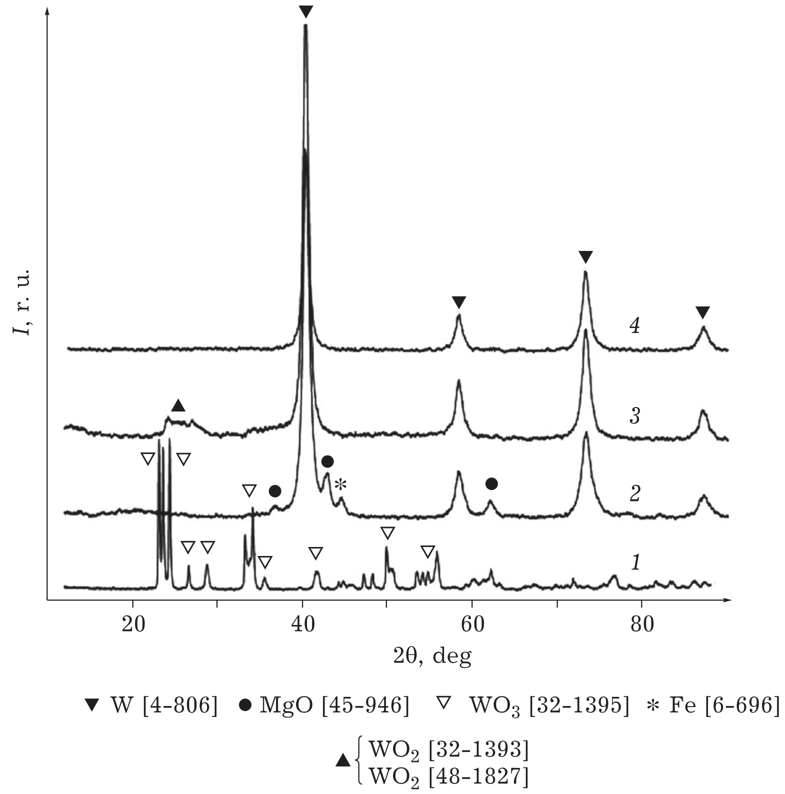

Fig. 3. Diffraction patterns of WO_3 samples before MA *(1)*, W/MgO mechanocomposites *(2)*, W/MgO mechanocomposite after MgO separation with a 1 M H_2SO_4 solution and water (3), tungsten after the treatment of W/MgO sequentially with a 1 M H_2SO_4 solution, water, 4 % solution of HF, water and acetone (*4*).

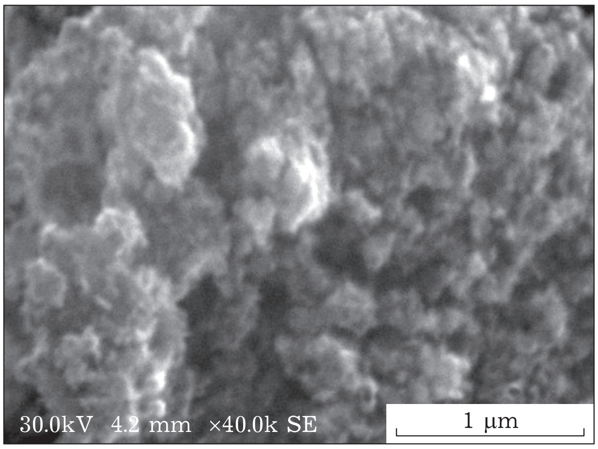

Fig. 4. Electron microphotograph of finely dispersed tungsten powder.

size (see Fig. 4). Magnesium content in tungsten powders as determined by means of EDS analysis was found to be less than 2 mass %.

The stability of the resulting fine tungsten during storage for 10 days under usual conditions is confirmed by the results of XRD.

CONCLUSION

Mechanochemical reduction of tungsten (VI) oxide by magnesium at the stoichiometric ratio of the components WO_3 / Mg = 1 : 3.6 and the frequency of cylinder rotation around the common axis 1000 r.p.m. is completed within activation for 8 min with the formation of W/MgO composite.

Consecutive treatment of the mechanochemical composite W/MgO with a 1 M H_2SO_4 solution and distilled water provides efficient separation of tungsten powder from magnesium oxide.

The removal of insignificant amount of tungsten oxides (VI–VI), formed in the presence of water and atmospheric oxygen at a temperature above 343 K, is achieved by consecutive treatment of the samples with 4 % solution of HF, water and acetone.

It was shown by means of scanning electron microscopy that tungsten powder is fine, composed of primary particles 50–100 nm in size, aggregated into secondary particles 1–10 μm in size.

The stability of mechanochemical composites W/MgO is conserved for 1 month, while fine tungsten isolated from the composites is stable not less than 10 days, which is confirmed by the results of XPA.

The magnesium content in fine tungsten powders was determined by means of energy-dispersive spectroscopy to be less than 2 mass %.

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REFERENCES

1 Kalamazov R. U., Tsvetkov Yu. V., Kalkov A. A., Ultrafine Powders of Tungsten and Molybdenum [in Russian], Moscow, Metallurgiya, 1988. 192 p.

2 Won C. W., Nersisyan H. H., Won H. I., Lee J. H., *Curr. Opinion Solid State and Materials Sci.*, 2010, Vol. 14, No. 3/4, P. 53–68.

3 Zhong S., Wen Y., Zhong H., *Powder Technol.*, 2014, Vol. 253, P. 128–132.

4 Pavlov E. A., Udalova T. A., Grigoreva T. F., Vosmerikov S. V., Vorsina I. A., Devyatkina E. T., Lyakhov N. Z., *Bull. RAS: Physics*, 2018, Vol. 82, No. 5, P. 574–577.

5 Udalova T. A., Grigoryeva T. F., Devyatkina E. G., Vosmerikov S. V., Lyakhov N. Z., *Chemistry for Sustainable Development* [in Russian], 2018, Vol. 26, No. 5, P. 537–543.

6 Schaffer G. B., McCormic P. G., *Metall. Trans. A*, 1990, Vol. 21, P. 2789–2794.

7 Shevchenko V. S., Investigation of exothermal mechanically stimulated reactions in oxide-sulphide systems (Candidate's Dissertation in Chemistry), Novosibirsk, 2003.

8 Grigoryeva T. F., Barinova A. P., Lyakhov N. Z., Mechanochemical Synthesis in Metal Systems [in Russian], Novosibirsk, Parallel, 2008. 310 p.

9 Raschman P., Fedoro¢ková A., *Hydrometallurgy*, 2004, Vol. 71, P. 403–412.

10 Busev A. I., Ivanov V. M., Sokolova T. A., Analytical Chemistry of Tungsten [in Russian], Moscow, Nauka, 1976. 240 p.

11 Urakaev F. H., Shevchenko V. S., Boldyrev V. V., *Doklady RAN*, 2001, Vol. 377, No. 1, P. 69–71.

12 Vagra M., Molnár Á., Mulas G., Mohai M., Bertóti I., Cocco G., *J. Catalysis*, 2002, Vol. 206, No. 1, P. 71–81.

13 Orlov V. M., Kolosov V. N., *Doklady RAN*, 2016, Vol. 468, No. 3, P. 288–292.

14 Miroshnichenko M. N., Kolosov V. N., Makarova T. I., Orlov V. M., *Izvestiya SPbGTI (TU)*, 2017, Vol. 38, P. 44–47.

15 Thermodynamic Properties of Individual Substances [in Russian], Reference book in 4 volumes, 3rd ed., V. P. Glushko (Ed.), Vol. IV, Elements Cr, Mo, W, V, Nb, Ta, Ti, Zr, Hf, Sc, Y, La, Th, U, Pu, Li, Na, K, Rb, Cs and Their Compounds, Book 1, Calculation of Thermodynamic Properties, Moscow, Nauka. 1982. 622 p.; Book 2, Tables of Thermodynamic Properties, Moscow, Nauka, 1982. 557 p.