



Using non-equilibrium state in the MoO_3 -H-C system for low temperature synthesis of ultradispersed molybdenum carbide powders

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Abstract

Pd additives and atomic hydrogen can accelerate kinetic processes in molybdenum reduction from molybdenum trioxide with hydrogen at 350°C in the presence of carbon. Such a low temperature reduction process (starting temperature 300–350°C) promotes the formation of a thermodynamically unstable nanodispersed phase with the specific surface area of 280 m²/g, which may be related to the formation of the intermediate cubic molybdenum suboxide Mo_{1-x}O , responsible for the preservation of the MoO_3 faceting. The specific surface area of 280 m²/g corresponds to the particle size ~3 nm. The phase transformation leading to the formation of Mo_2C in the MoO_3 -Pd-H₂-C system at a relatively low temperature (650°C) is the result of relaxation of the high free energy in the thermodynamically unstable system. The carbide formation process at such a low temperature yields carbide with the specific surface area from 4 to 40 m²/g (depending on the carbide-forming component), which can be easily sintered. The morphology of this carbide inherits the faceting of the initial whiskerous trioxide molybdenum. The microhardness of the sintered samples is significantly higher than that of carbide produced traditionally at high temperature.

Keywords: molybdenum, carbonization, reduction, nanosize

1. Introduction

In some cases, size effects begin to show up in the region of relatively large grain sizes. For example, the diffusivity, conductivity and mechanical properties of materials depend on the average grain size from its value 10^3 – 10^4 nm and with its decrease down to 10– 10^2 nm the melting temperature decreases and the lattice parameter changes. The most distinct size effect is observed in nanodispersed systems with a particle size of 1–10 nm. In this case, properties change drastically and a material may transform into a high temperature phase or another high energy state, which do not exist under standard conditions. The properties of nanodispersed systems are related to the peculiarities of atom-atom interaction, predominantly to the increased fraction of surface atoms in the total quantity of particle atoms [1].

Favourable conditions for obtaining nanosized powders of molybdenum via reduction from its ox-

ides comprise conducting the reaction under far-from-equilibrium conditions, keeping the temperature as low as possible and the fast removal of the products out of the reaction zone. These all together are beneficial for the enough high formation rate of new phase nuclei with simultaneous suppression of their growth. Molybdenum reduction with hydrogen from the trioxide MoO_3 over 500°C has been described in detail in literature. In particular, Lalik et al. [2] have established the existence of the orthorhombic Mo_4O_{11} phase as intermediate one between MoO_3 and MoO_2 at the reduction temperature 600°C. The thermodynamic calculations have shown that reduction processes in the MoO_3 -H₂ system are possible even at room temperature [3]. Using catalytic additives and atomic hydrogen allows one to solve the kinetic problems of intensifying processes of chemical interaction and to reduce the temperatures of both initial and final stages of reduction. It has been shown before that in the flow of hydrogen and hydrocarbons, MoO_3 transforms into MoO_xC_y [4].

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The present work deals with obtaining nanodispersed phases in the course of catalytic (in the presence of Pd) low temperature reduction of molybdenum with hydrogen and presents the results for using the non-equilibrium state in the $\text{MoO}_3\text{-H}$ system for the synthesis of ultradispersed molybdenum carbide powders. Also, the effect of the specific surface area (*SSA*) of the obtained molybdenum carbide on its further pressing and sintering has been studied.

II. Experimental

Molybdenum was reduced from molybdenum trioxide with the specific surface area of 0.4–0.5 m^2/g in a flow system using electrolytic hydrogen at a hydrogen flow of 500 cm^3/min . The molybdenum reduction was carried out under: i) low temperature conditions and stepped temperature rise from 200°C to 300–350°C and then to 500°C and ii) high temperature conditions at the initial temperature 500°C. As a catalyst, 0.01 wt.% Pd was introduced in the MoO_3 powder in the form of palladium chloride using an impregnation procedure. Black carbon with the *SSA* of 12 m^2/g was used as carbide-forming agents. In addition, in order to prevent oxidation of the obtained products, either hydrocarbons in the form of the propane-butane mixture $\text{C}_3\text{H}_8\text{-C}_4\text{H}_{10}$ or natural gas with the dominant component CH_4 was introduced into the reaction zone and heated to 600°C in hydrogen.

The degree of reduction was measured on a high-sensitivity balance with a quartz spiral. The *SSA* was determined using low temperature adsorption of nitrogen in the flow of nitrogen/helium mixture on (MPP2 unit, Sumperk, Slovakia). The change in the phase composition under the reduction was studied on an X-ray URS-55 unit in $\text{Fe } K_\alpha$ ($\lambda = 1.936 \text{ \AA}$) radiation. The composition of the gaseous phase was analyzed using a gas analyzer and a mass spectrometer (MKh-1302, firm “Ukrrospribor”, Ukraine). Total and bound carbon contents were determined using a chemical method of sample combustion in an oxygen flow. Oxygen was deter-

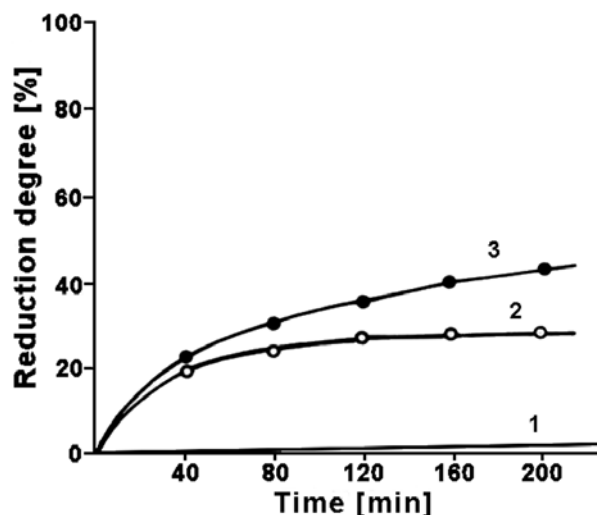


Figure 1. Kinetic curves of molybdenum reduction with hydrogen from MoO_3 at 350°C: (1) without catalyst, (2) in the presence of catalyst (palladium) and (3) in the presence of palladium and carbon

mined by the method of carbonizing melting in an inert gas flow under impulse heating of a sample with subsequent chromatographic separation of the extraction products using a gaseous chromatograph (LKhM-72, firm “Mosneftekip”, Russia) provided with a detector for thermal conductance. The morphology of different phases obtained via reduction and carbonization of molybdenum was examined using a scanning electron microscope (REM-200, firm “Electron”, Ukraine). Molybdenum carbide samples were pressed in the presence of plasticizer (rubber solution in benzene). Sintering was conducted in resistance and vacuum furnaces.

III. Results and Discussion

Processes of low-temperature reduction and carbonization of molybdenum in the presence of solid carbon

Molybdenum reduction from its trioxide at 350°C in both the presence and absence of solid carbon proceeds with a very low rate (Fig. 1, curve 1). Catalyt-

Table 1. Interplanar spacing (A) in products of low temperature reduction in the $\text{MoO}_3 + \text{H}_2$ system (reduction degree 84%) and carbidization (in different media and conditions)

Reference data		Propane-butane mixture, T=600°C, 8 min	Propane-butane mixture, Rising to 650°C	Propane-butane mixture, T=650°C, 2 h	Natural gas, Rising to 650°C
Molybdenum suboxide $\alpha^*=4.08$	Molybdenum oxycarbide $\alpha=4.14$				
2.36	2.396	2.36 Mo_{1-x}O	2.39 MoCO	2.60 Mo_2C	2.60 Mo_2C
2.04	2.075	2.04 Mo_{1-x}O	2.28 Mo_2C	2.36 Mo_2C	2.36 Mo_2C
1.44	1.464	1.44 Mo_{1-x}O	2.09 MoCO	2.28 Mo_2C	2.28 Mo_2C
1.23	1.250	1.23 Mo_{1-x}O	1.48 MoCO	1.75 Mo_2C	1.75 Mo_2C
1.17	1.195	1.17 Mo_{1-x}O	1.25 MoCO	1.50 Mo_2C	1.50 Mo_2C

*Note: α is the lattice parameter

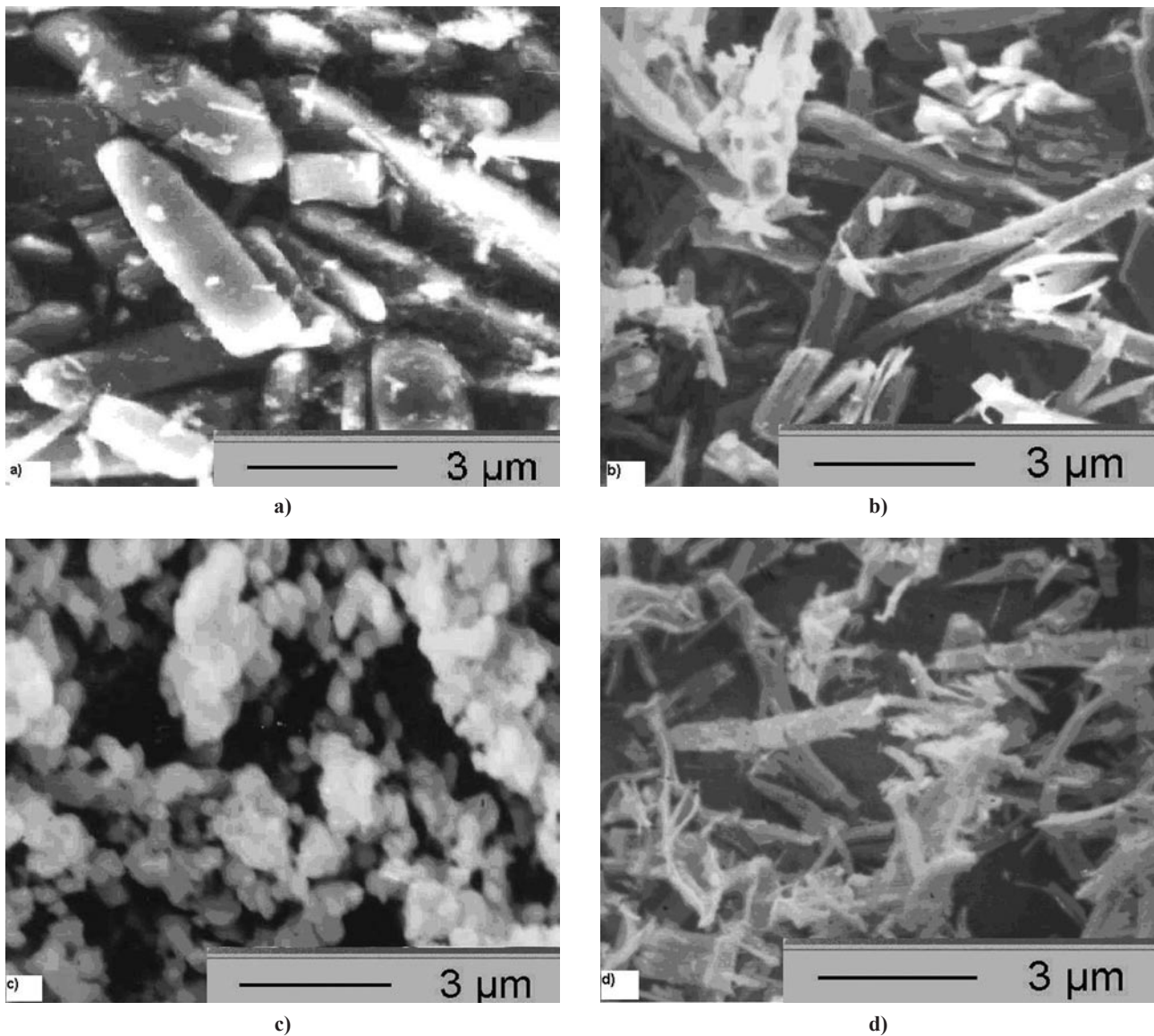


Figure 2. SEM photographs of: (a) initial MoO_3 , (b) $\text{Mo}_{1-x}\text{O}+\text{MoO}_2$ obtained at 350°C , (c) MoO_2 obtained at the initial reduction temperature 500°C , and (d) Mo_2C obtained using a low temperature reduction and carbonization

ic Pd addition promotes acceleration of the reduction (Fig. 1, curves 2 and 3). The slight increase in the reduction degree shown by curve 3 may be due to the presence of carbon. In the course of the catalytic reduction at 350°C in the presence of carbon, the liberated gas was analyzed. It contained H_2 (basic phase), CO , C_3O_2 , and C_2O_3 , which is evidence of the participation of solid carbon in the reduction process. However, its role as a reducing agent is insignificant. The X-ray analysis showed that in the presence of palladium under gradual temperature rise from 200 to $300\text{--}350^\circ\text{C}$, the unstable molybdenum suboxide Mo_{1-x}O with the cubic NaCl structure (Table 1) is formed in both cases, with and without of solid carbon; with the cubic phase line being more distinct in the former case. Thus, carbon may act predominantly as a stabilizer of the cubic phase. The X-ray data also showed that both at 350°C and under gradual temperature rise to 500°C , the MoO_2 phase is formed alongside with the cubic molybdenum suboxide Mo_{1-x}O phase. The appearance

of MoO_2 may be related to rebuilding of the crystalline lattice due the oxidation by the water vapour liberated during the reduction. The formation of the unstable Mo_{1-x}O phase at 350°C promotes preservation of both the initial MoO_3 particle shape (Fig. 2a,b) and high *SSA* at 500°C (Fig. 3). However, in the case of the high temperature reduction (initial temperature over 500°C), the faceting of the initial crystal is destroyed (Fig. 2c) and the *SSA* markedly decreases under the same reduction degrees (Fig. 4).

Therefore, the regime of stepped temperature rise $200\text{--}350\text{--}500^\circ\text{C}$ may be considered to be optimal for preservation of the initial orthorhombic MoO_3 faceting upon transition of the orthorhombic MoO_3 phase into the cubic Mo_{1-x}O . This transition leads to obtaining of high *SSA*, namely $280\text{ m}^2/\text{g}$, which may be related, on the one hand, to the difference in the volumes of these phases and, on the other hand, to the fact that the low temperature regime of catalytic reduction provides a high rate of nucleus formation alongside with a low rate of nucleus growth.

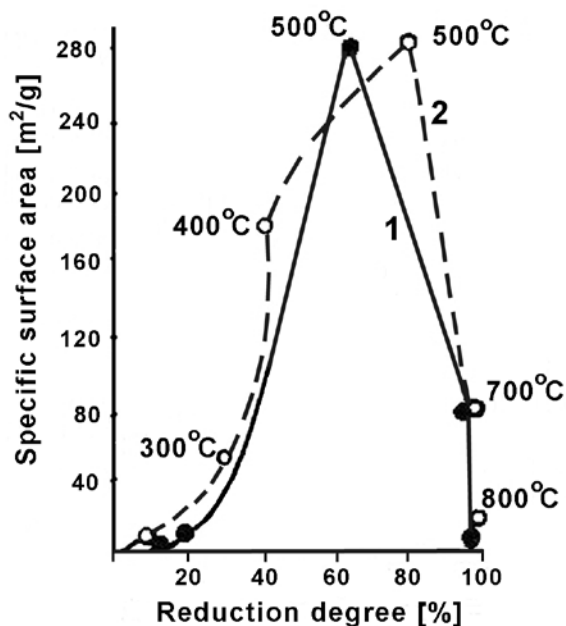


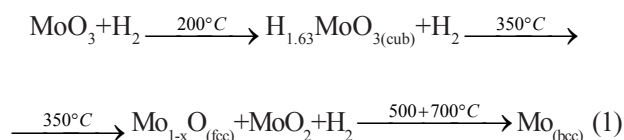
Figure 3. Dependence of the specific surface area on the reduction degree under low temperature reduction of molybdenum from the mixtures: (1) MoO_3+Pd and (2) $\text{MoO}_3+\text{Pd}+\text{C}$

Comparison of processes of surface development during molybdenum reduction from trioxide under low temperature conditions and stepped temperature rise from 200°C to 300–350°C and then to 500°C (Fig. 3) with those under high temperature reduction at the initial temperature 500°C (Fig. 4) showed that the *SSA* of the low temperature process products is lower by an order of magnitude. As follows from Figs. 3 and 4, the role of solid carbon in the reduction processes becomes evident at the beginning of the high temperature reduction, that is at 500°C, whereas under low-temperature conditions carbon does not affect the development of the *SSA* (Fig. 3, curves 1 and 2). The formation of the cubic molybdenum suboxide with a lattice parameter of 4.08 Å (both in the presence and the absence of carbon) makes it possible to conclude that there was no carbon in the molybdenum suboxide obtained, but the presence of carbon made the suboxide lines more distinct.

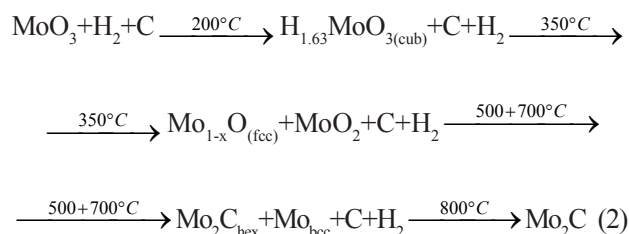
The particle size may be approximately calculated from the data on the *SSA* according to the equation $S = 6/d\rho$ [1], where d is the particle diameter and ρ is the substance density. At the *SSA* of 280 m²/g, the size of particles obtained at intermediated stages of the reduction is equal to ~ 3 nm. The free energy resource, ΔG_s , is estimated in the first approximation using the equation $\Delta G_s = \sigma_s S$ [1], where S is the total free surface of the system and σ_s is the surface tension, that is, the free energy resource correlates with S_{sp} and may be roughly estimated from the data on the *SSA*. It follows from the above mentioned that a system with the *SSA* of 280 m²/g has a greater resource of the free surface energy and is in a non-equilibrium state.

Therefore, it is interesting to investigate processes that can stabilize this state. In particular, combination of processes of reduction (using hydrogen) and carbonization (using carbide-forming agents such as black carbon, propane-butane mixture, natural gas, acetylene) in a continuous process seems to be promising.

A low temperature molybdenum reduction in the presence of palladium can be presented by the following scheme:



The yielded molybdenum has the *SSA* of 80 m²/g. It undergoes oxidation during the discharge. The presence of carbon changes this scheme as follows:



As a result of combination of the reduction and carbonization processes in the presence of solid carbon, ultradispersed molybdenum carbide with the *SSA* of 4 m²/g was produced. The chemical analysis showed that the contents of bound and free carbon in such a carbide were 6.0 and 0.1 wt.%, respectively. Figs. 2d and 5 demonstrate the surface topography and a X-ray im-

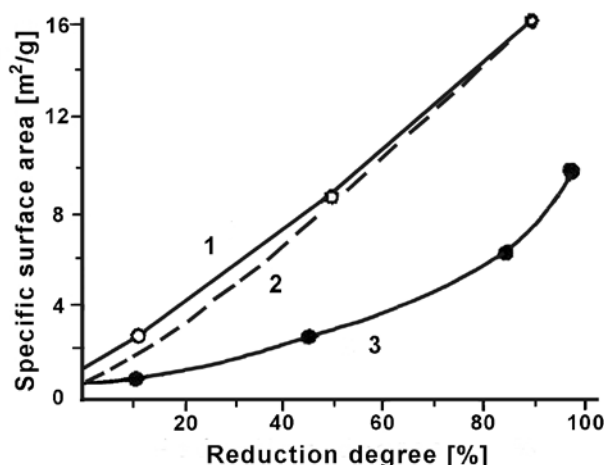


Figure 4. Dependence of the specific surface area on the reduction degree under high temperature reduction of molybdenum at 500°C from: (1) MoO_3+C , (2) MoO_3+C (minus the *SSA* of the C-black), and (3) MoO_3



Figure 5. X-ray image of Mo_2C obtained according to scheme (2) (see item 3.1)

age, respectively, of the molybdenum carbide powder obtained at 800°C. All of the obtained interplanar spaces correspond to the related reference data for Mo₂C.

Processes of reduction and carbonization in gaseous medium

In order to prevent oxidation of the obtained products, either hydrocarbons in the form of the propane-butane mixture C₃H₈-C₄H₁₀ or natural gas with the dominant component CH₄ was introduced into the reaction zone containing Mo_{1-x}O (reduction degree 84%) and heated up to 600°C in hydrogen. The data on the interplanar spacing of the products obtained after introduction of hydrocarbons in the reaction zone are listed in Table 1.

The X-ray analysis established that at 600°C, in the propane-butane medium, the cubic suboxide phase obtained under low temperature reduction conditions can be stabilized. The lines of other phases are not observed. At 650°C in the presence of propane-butane mixture, molybdenum suboxide transforms into molybdenum oxycarbide with a cubic type of the lattice and the hexagonal molybdenum carbide Mo₂C. With increasing both temperature and holding time, the process of transformation of the cubic oxycarbide phase into the hexagonal molybdenum carbide Mo₂C occurs. By the lattice structure, oxycarbide is close to molybdenum suboxide, but its lattice parameter is higher due to the introduction of carbon atoms. In terms of the latter process, the oxycarbide formation can be interpreted as a result of molybdenum suboxide saturation with carbon atoms from the gaseous hydrocarbon phase. The data of the chemical analysis of the oxycarbide phase obtained in the propane-butane medium showed that the content of bound oxygen varied from 6.5 to 10.5 wt.%, with the oxygen content changing from 5.8 to 3.5 wt.%. A general formula for oxycarbide obtained in this case can be written as Mo₃C_{2-x}O_x, where x=1.2–0.7 (corresponding to the oxygen content change from MoC_{0.76}O_{0.23} to MoC_{0.6}O_{0.4}). The oxycarbide phase with a lattice parameter of 4.15–4.18 Å,

which is isostructural with γ-Mo₂N, has also been revealed before in the course of investigation of molybdenum hexacarbonyls decomposition [5]. The MoO_{2.34}C_{0.1}H_{1.38} described in [4] and the Mo₃C_{3-x}O_x obtained in the present work significantly differ in the content of oxygen: the reduction degree for MoO_{2.34}C_{0.1}H_{1.38} is 20% whereas for Mo₃C_{3-x}O_x (x=1.2–0.7) it is 90%. The structure of Mo₃C_{3-x}O_x is close to that of the metastable cubic molybdenum carbide Mo_xC_y. Herein oxygen behaves as a stabilizer of the cubic phase. An increase in the annealing time to 2 h facilitates the transformation of the cubic phase with a lattice parameter of 4.15–4.18

Å into the hexagonal molybdenum carbide Mo₂C. The SSA of the obtained Mo₃C_{3-x}O_x carbide attained 40 m²/g, which corresponds to a particle size of 15 nm (in accordance with the equation $S = 6/d\rho$).

Boskovic et al. [6] have concluded that the intermediate products of MoO₃ activation in an H₂-CH₂ atmosphere can be used for paraffins isomerization. The obtained in the present work oxycarbide Mo₃C_{3-x}O_x may be considered as a promising catalyst for the same purpose.

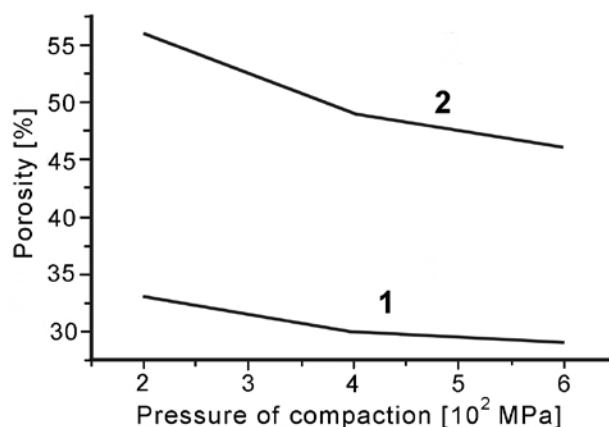


Figure 6. The dependence of the porosity on the compaction pressure for Mo₂C powders with different SSA: (1) 0.1 m²/g and (2) 4.0 m²/g

Table 2. Sintering ability of molybdenum carbide of different dispersity and microhardness of sintered samples

SSA of Mo ₂ C [m ² /g]	Starting sample	Porosity [%]			Microhardness, [kg/mm ²]
		Sample sintered in vacuum at		Sample sintered in resistance furnace at	
		1700°C	1850°C	1300°C	
4	57	8	3	18	2200
4	55	7	8	13	2200
4	49	7	7	11	2200
0.1	30	18	17	25	1470 [7]

Table 3. The wear intensity of the obtained coatings in comparison with that of known uncoated materials

Composition	Wear intensity [μm/min]
Ni-B+Mo ₂ C	70
Ni-B+ (Mo ₂ C + TiC)	10
WC15Co	40
Hardened steel 45	520

Forming and sintering of ultradispersed molybdenum carbide

Densification of ultradispersed molybdenum carbide with the SSA of 4 m²/g is substantially worse compared to that of commercial molybdenum carbide powder with the SSA of 0.1 m²/g obtained via carbonization of molybdenum powder at 1500°C (Fig. 6, curve 1). Ultradispersed powders have a developed surface, which makes densification difficult whereas looser commercial powders are compacted much better.

Sintering of molybdenum carbide of different SSA was studied on samples compacted to different porosity. The temperature dependence of the porosity of the sintered samples is presented in Table 2.

The abrasive ability of molybdenum carbide with a SSA of 4 m²/g

Addition of 40 wt.% of the obtained molybdenum carbide with the SSA of 4 m²/g to diamond pastes and suspensions used for polishing the working zones of draw dies resulted in increasing the abrasive ability by 20% and reducing the roughness of the surface under processing by one grade. The abrasive ability was determined from the ratio of the mass lost by the corundum samples to that of the diamond powder used for 60 min. The use of diamond suspensions with a Mo₂C filler characterized by the SSA of 4 m²/g made it possible to increase the efficiency of processing by 8 times.

In order to determine the abrasion resistance of galvanic-phoretic Ni-B-Mo₂C coatings containing ultradispersed Mo₂C, the wear intensity of the coatings was studied using a diamond wheel and a friction test unit MT-22 at a sliding velocity of 1 m/s and a load of 0.3 MPa. The wear intensity of the coatings was compared to that of the solid alloy WC15Co and hardened steel 45. The obtained results are presented in Table 3.

The tests demonstrated that under the conditions of corrosion/erosion wear the service life of dispersing mixer parts strengthened with galvanic-phoretic Ni-B+Mo₂C coatings is 4–5 times longer than that of parts from 10Cr18Ni9Ti steel.

VI. Conclusions

- In the course of low temperature molybdenum reduction, non-equilibrium nanodispersed phases with a high specific surface area (high resource of free energy) are formed.
- Combination of processes of reduction and carbonization in a continuous process is proposed as a mean for the free energy relaxation.
- Low temperature reduction of molybdenum in the presence of carbide-forming agents promotes the formation of nanodispersed carbides and oxycarbides.
- Molybdenum carbide with the specific surface area of 4 m²/g can be sintered to the porosity 3% while under the same sintering conditions the porosity of molybdenum carbide with the specific surface area of 0.1 m²/g is equal to 17%.
- Microhardness of sintered dispersed molybdenum carbide is 2200 kg/mm² (for comparison, that of commercial products is 1470 kg/mm²).

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