
STRUCTURE, PHASE TRANSFORMATIONS,
AND DIFFUSION

Microstructure and Properties of Surface-Modified Tungsten Powders Mechanically Activated in Different Media

V. I. Savenko*, Yu. P. Toporov, V. V. Chernyshev, and A. I. Malkin

*Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences,
Moscow, 119071 Russia*

**e-mail: visavenko@rambler.ru*

Received November 18, 2016; in final form, March 3, 2017

Abstract—The results of an experimental-theoretical study of the effect of thin-film coatings on residual microstrains, microstresses, and local microdistortions of the atomic structure of powder tungsten mechanically activated in the centrifugal ball mill have been presented. It has been shown that microdistortions of the crystal structure of different system-hierarchical levels arise in the surface-oxidized powders, which increase with an increase in the time of the activation process. It has been shown that this should lead to a significant increase in the reactivity of the mechanically activated powder tungsten. In contrast, the adsorption films that plasticize the near-surface layer of particles can decrease the efficiency of the mechanoactivation process of the tungsten powder.

Keywords: powder tungsten, mechanical activation, microstresses, microstrains, rate constant of chemical reaction, surface films, Rehbinder effect

DOI: 10.1134/S0031918X17110138

INTRODUCTION

Surface-active substances (SAS) and thin-film coatings significantly affect the mechanical characteristics of metals and change the yield stress, strengthening coefficient, and ultimate strain of the material, which is one of the forms of the Rehbinder effect [1–3]. In the metallic samples coated by films of foreign metals, oxides, or SAS, internal residual stresses arise after plastic deformation, the sign and space distribution of which depend not only on the loading scheme and type of the stress–strain state of the material, but also on the presence and type of a surface film that controls the yield stress of its near-surface layer [4–6].

The mechanoactivation of the metallic powders by the treatment in planetary-centrifugal mills (PCMs) is one of the most effective and widely used methods of the energy-power action on the powders [7]. The tungsten powders (with particles of micron sizes) are widely used upon preparation of the energy-saturated functional materials of a new generation with given physicochemical and thermodynamic characteristics by the mechanoactivation methods with the application of PCMs. The boundary conditions, including the surface state of the powder particles subjected to mechanical action, play a key role in the achievement of these characteristics [6, 7]. The present paper is aimed at studying the effect of thin-film coatings of a different nature on the residual stresses and strains, which arise in tungsten powders upon their mechano-

activation with the application of the PCM-treatment method. Some thermodynamic properties of these powders were analyzed.

EXPERIMENTAL

The tungsten powders of PV-2 grade of industrial production were subjected to tests. An average size of particles in powders was 2 μm . Two types of powders were studied. The particles of powders of the first type were coated by a natural oxide film with a thickness of 30–60 nm, the hardness and yield stress of which are lower than that of the metal of the intrabulk region [8, 9]. Nevertheless, the presence of the film significantly strengthened a near-surface layer of particles due to the inhibition of the processes of motion and multiplication of the near-surface dislocations in the tungsten lattice and in other refractory metals [10, 11]. The thickness of this strengthened near-surface layer of the tungsten particles was 0.2–0.4 μm [11, 12].

The powders of the second type were surface-modified; they were coated by a solid-like adsorption film of an SAS, which was formed by the deposition of molecules of the perfluoropolyether carboxylic acid (PFPECA) on the surfaces of particles. The near-surface layer of the particles of this powder was plasticized to a depth of several tens nanometers; it had a yield stress that was significantly lower than that of the material of the intrabulk region of the particles [1–6, 12].

Both types of powder samples were subjected to mechanoactivation at a centripetal acceleration of 300 m/s^2 in an AGO-2U planetary ball mill equipped with containers (water-cooled drums) loaded with powder samples and milling balls with a diameter of 8 mm, which were produced from an ShKh15 steel. The relation between the weight of the powder and the weight of the balls was 1 : 10. The time of the mechanoactivation process was varied in the range of 3–50 min.

The regimes of activation were chosen based on the previous studies [7].

The mechanoactivation of the powders of the surface-oxidized particles was carried out in an inert medium (heptane, hexane, or freon) and in air. Powders coated with adsorption films of SAS were mechanically activated in surface-active media, namely, in solutions of PFPECA in freon with different concentrations. The crystal structure of the powder particles was determined using an analysis of the X-ray diffraction patterns, which were obtained upon X-ray studies of the samples at room temperature ($T = 22^\circ\text{C}$) using Stoe Huber G670 and Emyrean diffractometers with a Guinier camera in the reflection geometry (monochromatized $\text{Cu } K_\alpha$ radiation, nickel filter, corundum substrate). In calculations, we took into account two wavelengths, i.e., 1.5406 and 1.5444 Å, with a line intensity ratio in the doublet equal to 2 : 1. The measurements were carried out in the range of reflection angles of $2\theta = 5^\circ\text{--}120^\circ$ with a step of 0.0334° .

Using the X-ray diffraction patterns obtained and standard methods [13, 14], the unit cell parameters a , the sizes of microblocks D (domains of coherent X-rays scattering, CDs), and magnitudes of microdistortions and microstresses of I, II, and III kinds in the crystal structure of the initial and mechanically activated samples were determined. In all cases, the refinement of the calculation results was carried out by the Rietveld method [15] using MRJA software [16]. The reliability of the refined results was estimated based on an agreement criterion using the χ^2 distribution [17]. For all of the analyzed variants, the values of χ^2 fluctuated in the range of 0.9–6 and; in rare cases, reached 9, which indicates the acceptability of the used approximations.

According to the results of the procedure of the full-profile refinement of the obtained characteristics [18], we calculated the corrected values of the lattice parameter a and the average values of the quantity $\langle U_{\text{iso}}^2 \rangle = \langle U_{\text{st}}^2 \rangle + \langle U_{\text{din}}^2 \rangle$, which is total characteristic of static $\langle U_{\text{st}}^2 \rangle$ and dynamic $\langle U_{\text{din}}^2 \rangle$ deviations of atoms from their equilibrium positions in the sites of the crystal structure for both the initial samples and the samples subjected to mechanical activation at different processing times t .

The determination of the sizes of microblocks D of the crystal structure and the magnitudes of microdis-

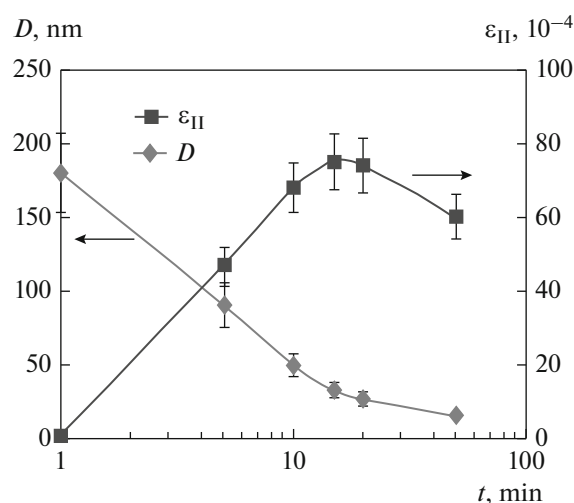


Fig. 1. Dependences of average size D of microblocked structure and magnitude of microdistortions of the second kind ε_{II} in the crystal structure of the oxidized particles of tungsten on the time of mechanoactivation t of powdered samples in pure hexane.

tortions of the second kind $\varepsilon_{\text{II}} = \Delta d/d$ in the material was also carried out according to the results of the refinement of the full-profile analysis of the form of Debye reflections [18] in the X-ray diffraction patterns using a HighScore software.

RESULTS AND DISCUSSION

It has been detected that the mechanoactivation of the surface-oxidized particles, which was performed in air or in an inert medium, is accompanied by a decrease in the sizes $D(t)$ of the microblocked structure and by an increase in the microdistortions ε_{II} of the second kind in the crystal structure of tungsten, which increase with increasing time t of processing (Fig. 1). At the same time, an increase is observed in the values of the total $\langle U_{\text{iso}}^2 \rangle$ and, consequently, of the static $\langle U_{\text{st}}^2 \rangle$ microdistortions of the third kind. Here, it should be noted that the equivalence of the changes in these characteristics in these experiments is due to the fact that the magnitude of $\langle U_{\text{din}}^2 \rangle \approx 2.4 \times 10^{-6} \text{ nm}^2$ is significantly smaller than $\langle U_{\text{st}}^2 \rangle$ and is not changed in the isothermal experiments). With increasing time of the mechanoactivation of particles of the oxidized powder, a decrease in the magnitude of the lattice parameter a is also observed (Fig. 2).

The increase in the microdistortions of the second and third kinds causes the appearance of microstresses of the second and third kinds in the crystal structure of the material. A decrease of a occurs due to the appearance of the internal residual compressive macrost-

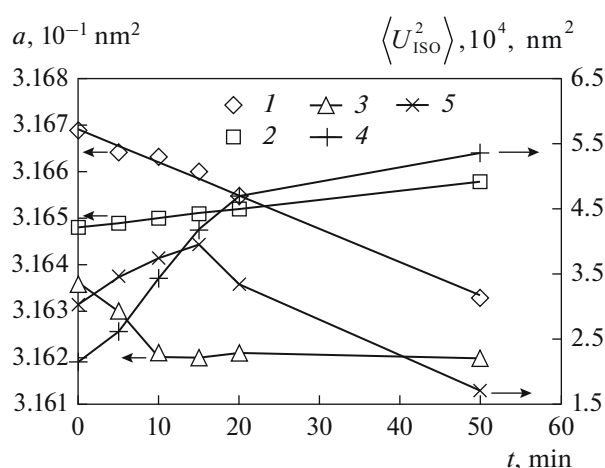


Fig. 2. (1–3) Dependences of lattice parameter a and (4, 5) magnitude of $\langle U_{ISO}^2 \rangle$ on the time of the mechanoactivation t of the tungsten powders, particles of which were (1, 4) coated by the oxide film and mechanically activated in air, (2, 5) coated by a film of an SAA and mechanically activated in the solution of PCA, and (3) coated by an oxide film and mechanically activated in pure hexane.

resses (of the first kind) in the material located in the intrabulk region of particles. Upon the mechanoactivation of the particles surface-oxidized in the air atmosphere, the intensity of these phenomena increases compared to the inert medium.

The main but possibly not the only source of compressive macrostresses is a near-surface oxide-film-strengthened layer of the material of particles, which was elastoplastically deformed upon mechanoactivation. The thickness of this layer is particularly greatly increased due to the additional intensive oxidation of the surface layer of the powder particles upon their mechanoactivation in an air atmosphere. Upon the mechanoactivation of the powder in an inert medium (e.g., in pure hexane), the oxidation processes are much less intensive, and these effects are less pronounced.

In accordance with the conditions of the mechanical equilibrium, after the mechanoactivation of this material, the compensating tensile macrostresses (also of the first kind) should appear in the surface oxide film and in the near-surface layer of particles strengthened by this film [4–6]. However, because of an extremely small thickness of these layers, the X-ray diffraction reflections that correspond to them in these experiments were below the background level and the magnitude of the tensile stresses in these layers could not be experimentally determined using this method.

The presence of an absorption film of PFPECA at the surface of the mechanically activated powder dramatically changes the character of the structure evolution that occurs upon the mechanoactivation in the

material of the particles. In this case, after the mechanoactivation of the powder, a progressing increase in the lattice parameter of tungsten is observed with increasing time of activation (Fig. 2, curve 2), which indicates the uniform extension of the material in the intrabulk region of particles. As was shown earlier [4–6], the reason for the appearance of the residual deformations of this sign in the material after energy-power action on the particles in the case of the centrifugal ball milling (which corresponds to the ‘compression + shear/tension’ deformation scheme of the material [7]) is the earlier onset of the stage of the plastic deformation of the material in the near-surface plasticized layer of particles as compared to their intrabulk regions. As a result, upon the unloading of the material, residual compressive macrostresses (of the first kind) appear in this layer; in the bulk regions of the powdered particles, compensating tensile macrostresses of the same kind arise [4–6].

Under the conditions of mechanical equilibrium, the ratio of the levels of these stresses should obviously be inversely proportional to the average values of the areas of sections of the corresponding regions of the particle. The approximate quantitative estimates, which are based on the generalized (tensor) Hooks law for an isotropic medium $\sigma_{ii} = 3K\varepsilon_{ii} = [E/(1-2\nu)]\varepsilon_{ii}$ and, for the averaged values of the tensile stresses of the material in the intrabulk region of the particles after the mechanoactivation of the powder for $t = 50$ min, based on the data presented in Fig. 2, we have the following values: $\langle \sigma_{ii}(50) \rangle_{in} = \langle \varepsilon_{ii}(50) \rangle_{in} E / (1-2\nu) = [\Delta a(50)/a] E / (1-2\nu) \approx -0.22$ GPa. Here, σ_{ii} , (ε_{ii}) is a convolution (trace) of the diagonal components of the stress (strain) tensor, K is the modulus of the uniform compression of tungsten, $E = 355$ GPa is its Young’s modulus, and $\nu = 0.27$ is the Poisson’s coefficient [19].

Taking into account the ratio of the areas of the cross sections of the intrabulk region of the particle and its plasticized near-surface layer, which were averaged over the ensemble of particles, $S_{in} : S_{ex} \approx 10 : 1$, we obtain for the compressive residual stresses in this layer: $\langle \sigma_{ii}(50) \rangle_{ex} = (S_{in}/S_{ex}) \langle \sigma_{ii}(50) \rangle_{in} \approx +2.2$ GPa. A similar approach upon estimating the residual stresses of compression and tension in the corresponding structural constituents of the surface-oxidized material after its mechanoactivation gives $\langle \sigma_{ii}(50) \rangle_{in} \approx +0.88$ GPa and $\langle \sigma_{ii}(50) \rangle_{ex} \approx -8.8$ GPa.

The dependences of the microstrains and microstresses of the second kind in the surface-oxidized and -plasticized powders on the time of their mechanoactivation vary nonlinearly, but almost symbatically to each other, demonstrating maxima at the process times $t \approx 10$ –15 min. The total level of values of ε_{II} for surface-oxidized powders is significantly less than that for surface-plasticized powders. The estimate of the amplitude of the residual microstresses of the second

kind for oxidized powder mechanically activated for 15 min, in the material of which the microdistortions of this kind reach the maximum level, gives the following values: $\sigma_{II}(15) \approx E\varepsilon_{II}(15) = 2.6$ GPa. In the material of powders mechanically activated for more prolonged times, microstrains and microstresses of this kind are somewhat decreased. In oxidized material mechanically activated for 50 min (Fig. 1), $\sigma_{II}(50) \approx 2.1$ GPa. The latter circumstance is apparently associated with a progressive decrease in the average sizes of the powder particles and the intensification of the processes of dynamic recovery in the material during its too long mechanoactivation.

As was already mentioned, the deviations of atoms from their equilibrium positions in the crystal-lattice sites characterized by the magnitude $\langle U_{st}^2 \rangle$, cause the appearance of locally distributed (with a radius on the order of a) internal residual microstresses of the third kind in the material. Their amplitude can be approximately estimated in accordance with the relation $\sigma_{III} = E(\langle U_{st}^2 \rangle)^{0.5}/a$. The amplitudes of these stresses are $\sigma_{III}(50) \approx 9.6$ GPa for the surface-oxidized powders mechanically activated for $t = 50$ min and $\sigma_{III}(50) \approx 7.8$ GPa for the surface-plasticized powders. It should be noted that in the last case, the time dependence $\langle U_{st}^2 \rangle = f(t)$ of the magnitude of microdistortions varies symbatically to the $\varepsilon_{II}(t)$ dependence for oxidized powders. These dependences reach their maximums at the same activation time $t = 15$ min (compare Figs. 1 and 2). Obviously, the reasons for the simultaneous decreasing of the numerical values of these characteristics under more significant times t of mechanical activation of the powders are also the processes of dynamic “returning” or “restoring” that occur in the surface-plasticized material at times of the mechanoactivation $t > 15$ min.

A comparison of the obtained values of the residual stresses of different system-hierarchical levels with the magnitude of the macroscopic (without taking into account the scale factor) ultimate tensile strength σ_u of metallic tungsten of -4 to -10 GPa [19] leads to the fact that, in all cases, the powder particles are in the state of prefracture after mechanoactivation. However, upon the possible further (at $t > 50$ min) energy-power action on the particles of the surface-oxidized powder, the oxide film coating the particles and their near-surface strengthened layer will primarily become destroyed; on the contrary, upon the mechanoactivation of the surface-plasticized powder, this will be the material of the intrabulk regions of particles. It is obvious that, in the last case, at fairly long times of the mechanoactivation $t > 50$ min, a more intensive refinement of the powder particles will be observed. Thus, the use of surface-active media upon mechanoactivation, can lead to a substantial increase in the level of the dispersity of the tungsten powder. Our numerous experi-

ments of the refinement of metallic materials with the use of SAS confirm this conclusion [20].

It is obvious that, according to the kinetic theory of strength [21], similar processes will occur upon the prolonged storage of powders mechanically activated at $t \geq 50$ min.

The mechanoactivation of metallic powders is often applied in different technological schemes to increase their reactivity as reagents in heterophase chemical reactions. As a result of the preliminary mechanoactivation of these reagents, the rate of corresponding chemical and quasichemical reactions that occur at a given temperature increases, or the processing temperature at a given fixed rate decreases. (In this case, it is understood that upon realization of the process in the second variant, the powder mixture is almost immediately heated to a given reaction temperature to avoid the annealing of the material upon its gradual heating).

It can easily be shown that, for the ratio of the constants K that control the rate of the bimolecular heterophase permutoid chemical reaction that occurs at the same temperature T , but with the use of the non-activated reagent and the reagent activated in the inert medium, the following relationship is fulfilled [22]:

$$K_{\text{activ}}(t)/K_0 = \exp\left\{-\delta(\Delta H) + 0.5E[\delta\langle U_{st}^2 \rangle/a^2] + (\Delta a/a)^2 + (\Delta d/d)^2 + T\delta(\Delta S)\right\}/RT. \quad (1)$$

Here, R is the universal gas constant; the term $\delta(\Delta H) = (\Delta H_{\text{activ}} - \Delta H_0) = (H_{\text{activ}} - H_0)$ shows the variation of the enthalpy of the system upon its mechanoactivation, which is caused by an increase in the concentration of linear and point defects in the crystal material; and $\delta(\Delta S) = \delta(\Delta S_{\text{activ}} - \Delta S_0) = S_0 - S_{\text{activ}}$ is the variation in the entropy factor, which is caused by the transformation of the phonon spectrum of the tungsten crystal structure under the action of mechanoactivation. Upon the derivation of these relations, it was assumed that the values of the entropy, enthalpy, and specific volume of the activated complex characterizing the thermally excited state of the system upon the chemical reaction are not changed under the action of the mechanoactivation. In the considered model, it is assumed that, as a result of the mechanoactivation, only the initial values of the enthalpy, entropy, and inner energy, which characterize the state of the system prior to the onset of the chemical reaction, are changed. It is obvious that the values of all terms that are in the numerator of the exponent (1) will depend on the time of the mechanoactivation of the powder.

As an example, let us estimate the contributions of the above-mentioned constituents for a surface-oxidized powder mechanically activated for 15–20 min, the characteristics of which have the most significant contribution to the expression (1) and reach the maximum level. The numerical values of the characteris-

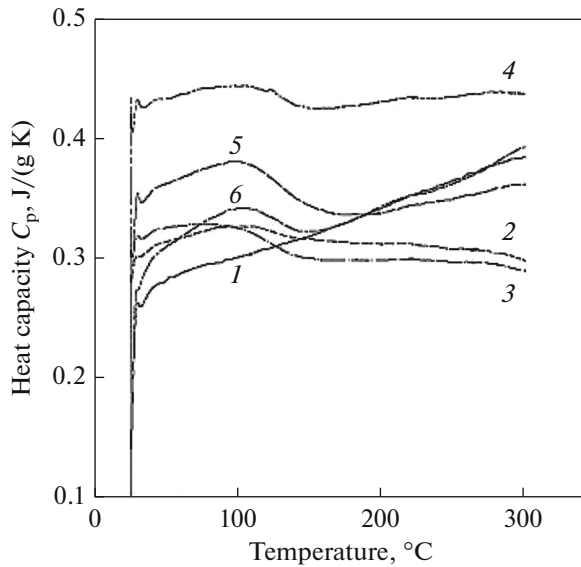


Fig. 3. Temperature dependence of the heat capacity of the surface-oxidized powdered tungsten: (1) initial and (2–6) subjected to the mechanoactivation in pure hexane for (2) 5, (3) 10, (4) 15, (5) 20, and (6) 50 min [23].

tics required for these calculations were taken from the graphs presented in Figs. 1–3.

The simple calculation shows that the density of the energy of stresses of the first kind is $W_I = 0.5E(\Delta a/a)^2 \approx 10$ J/mol; the densities of the energy of microstresses of the second and third kinds are $W_{II} = 0.5E(\Delta d/d)^2 \approx 10^2$ J/mol and $W_{III} = 0.5E[\delta(U_{st}^2)/a^2] \approx 10^3$ J/mol, respectively.

The calculation of the change in the entropy factor $\delta(\Delta S)$ can be performed based on changes of the heat capacity of the powder as a result of its mechanoactivation, which are presented in Fig. 3 [23]. Since the Debye temperature of tungsten is $T_D = 310$ K, the high-temperature approximation can be used to estimate the heat capacity C_p and the entropy of the powder at temperatures of the possible occurrence of chemical reactions as follows [24]:

$$C_p \approx R \left[1 - 0.05 \left(\frac{h\varpi}{k_B T} \right)^2 \right]; S \approx R \left[1 - \ln \left(\frac{h\varpi}{k_B T} \right) \right]$$

$$\text{and } \frac{\partial C_p}{\partial T} \approx \frac{0.1R}{T} \left(\frac{h\varpi}{k_B T} \right)^2,$$

where $\ln \varpi = \frac{1}{3N} \sum_{\alpha=1}^{3N} \ln \omega_{\alpha}$. Here, k_B and h are the Boltzmann and Planck constants, respectively; ω_{α} is the oscillation frequency of the normal oscillator with the order number α in the phonon spectrum of the crystal structure, which contains the frequencies of $3N$ normal oscillators. In the case of the continuous fre-

quency spectrum, the transition to integration on the right-hand side of the last expression is performed.

Taking into account that, at $T > 400$ K, there takes place an intensive annealing of the crystal-structure defects in the material of mechanically activated tungsten powders, the calculations of the heat capacity in the region of the relatively high temperatures should be limited to the extrapolation of values of the heat capacity, which are observed at relatively low temperatures $T \leq 400$ K, to these temperatures (Fig. 3). Then, upon comparative tests of the reactivity of the mechanically activated (for $t = 15$ min, index activ) and nonactivated (index 0) powder samples at the same temperature T , we have

$$\left(\frac{\partial C_p}{\partial T} \right)_{\text{activ}} = \left(\frac{\langle \omega_{\text{activ}} \rangle}{\langle \omega_0 \rangle} \right)^2 \approx 0.5 \quad \text{and} \quad \frac{\langle \omega_{\text{activ}} \rangle}{\langle \omega_0 \rangle} \approx 0.7.$$

Therefore

$$\delta(\Delta S) = S_0 - S_{\text{activ}} = R \ln \frac{\langle \omega_{\text{activ}} \rangle}{\langle \omega_0 \rangle} \approx -0.36R.$$

The estimation of the quantity $\delta(\Delta H)$ in this approximation according to the data of Fig. 3 (curves 1 and 4) gives $\delta(\Delta H) = (C_{\text{activ}} - C_0)\Delta T \approx 9.2\Delta T$ J/mol; the magnitude of ΔT is determined by the difference between the temperature of the possible chemical reaction and the temperature of the onset of the mechanoactivation of the powder (in this case, close to room temperature).

The substitution of the found values of the above-mentioned characteristics into the relationship (1) leads to the desired relationship at $\Delta T \approx 10^3$ K with the following functional dependence on the reaction temperature:

$$[K_{\text{activ}}(50)/K_0]_{\text{ox}} \approx \exp[+(8 \times 10^2/T)]. \quad (2)$$

In the case of the bimolecular chemical reactions that occur at $T \approx 10^3$ K, the magnitude of $[K_{\text{activ}}(50)/K_0]_{\text{ox}} \approx 2.2$ and the reaction rates when using the activated powder (under other equal conditions) will increase by about 200%.

When selecting the equal-rate regime, the temperature of the occurrence of the reaction can be decreased significantly. In fact, in the total case for bimolecular heterophase permutoid reaction, the following relation is valid for the reaction-rate constant K [21]:

$$K = \left(\frac{k_B T^2}{h} \right) \exp \left(-\frac{E_{\text{eff}}}{RT} \right)$$

$$= (k_B/h) \exp \left[(2 \ln T) - \frac{E_{\text{eff}}}{RT} + 1 \right].$$

Then, for the ratio of the constants K of the reactions that occur using the mechanically activated and non-

activated powder, the following functional dependence takes place:

$$\frac{K_{\text{activ}}}{K_0} = \exp \left[2 \ln \left(\frac{T_{\text{activ}}}{T_0} \right) - \frac{E_{\text{eff}}^{\text{activ}}}{RT_{\text{activ}}} + \frac{E_{\text{eff}}^0}{RT_0} \right]. \quad (3)$$

Taking into account that, for these reactions, the relationship $E_{\text{eff}}^{\text{activ}} - E_{\text{eff}}^0 = \beta RT_0$ should be fulfilled, where

$$\left\{ \begin{aligned} \beta &= -\delta(\Delta H) + 0.5E[\delta(\langle U_{\text{st}}^2 \rangle / a^2 \\ &+ (\Delta a/a)^2 + (\Delta d/d)^2] + T\delta(\Delta S) \end{aligned} \right\}, \quad (4)$$

we have

$$\frac{K_{\text{activ}}}{K_0} = \exp \left[2 \ln \left(\frac{T_{\text{activ}}}{T_0} \right) - \frac{E_{\text{eff}}^0 - \beta RT_0}{RT_{\text{activ}}} + \frac{E_{\text{eff}}^0}{RT_0} \right]. \quad (5)$$

In the case of the equal-rate regime of the reaction, we have $\frac{K_{\text{activ}}}{K_0} = 1$; then,

$$2 \ln \left(\frac{T_{\text{activ}}}{T_0} \right) - \frac{E_{\text{eff}}^0 - \beta RT_0}{RT_{\text{activ}}} + \frac{E_{\text{eff}}^0}{RT_0} = 0. \quad (6)$$

Assuming that the temperatures T_{activ} and T_0 are close by the order of magnitude and using the approximation $\ln \frac{T_{\text{activ}}}{T_0} \cong \frac{T_{\text{activ}}}{T_0} - 1$, after simple mathematical transformations, we obtain the following quadratic equation relative to $\frac{T_{\text{activ}}}{T_0}$:

$$2 \left(\frac{T_{\text{activ}}}{T_0} \right)^2 - \left(\frac{T_{\text{activ}}}{T_0} \right) \left(\frac{E_{\text{eff}}^0}{RT_0} - 2 \right) - \left(\frac{E_{\text{eff}}^0}{RT_0} - \beta \right) = 0. \quad (7)$$

At a given value of β , the solution to this equation is determined by the magnitude of the ratio $\frac{E_{\text{eff}}^0}{RT_0}$.

Assuming that $\frac{E_{\text{eff}}^0}{RT_0} \approx 2-4$ for the chemical reactions that occur on the nonactivated surface-oxidized powder with a fairly high and, taking into account the fact that we consider reactions that involve this powder at $T_0 \approx 10^3$ K, we obtain from the solution of Eq. (7) that, for the value $\beta = 0.8$ determined in accordance with relationship (4), the ratio $\frac{T_{\text{activ}}}{T_0} \approx 0.8$.

Similar calculations carried out for the surface-plasticized films of the PFPECA powder mechanically activated in the presence of SAS show that, in this case, there is a slightly different picture. The ratio of constants K is expressed now by the temperature function

$$[K_{\text{activ}}(50)/K_0]_{\text{plast}} \approx \exp [(3 \times 10^{+2}/T)], \quad (8)$$

and the rates of the corresponding reactions occurring, as before, at $T \approx 10^3$ K increase only by 20–30%.

Nevertheless, in the case of the using of a surface-plasticized reagent, the rate of the corresponding chemical reaction can still increase much more due to a significant increase in the specific surface of the tungsten powder because of its greater refinement upon mechanoactivation in medium containing SAS.

Upon the use of the equal-rate regime for a chemical reaction that occurs at a temperature of $T = 10^3$ K, but with the application of the surface-plasticized powder at $\beta \approx 0.3$ (relations (3)–(5)), the reaction temperature can be decreased in accordance with the relation $\frac{T_{\text{activ}}}{T_0} \approx 0.9$. In this case, a decrease in the temperature is less than that upon the use of the surface-oxidized powder.

The use of this approach to analyzing the behavior of the surface-oxidized powder of tungsten, which was mechanically activated in pure hexane, yields an intermediate result between the above-considered cases.

CONCLUSIONS

(1) It has been found that the mechanoactivation of the surface-modified powders of tungsten in different media leads to a significant change in its microstructural characteristics, which causes the appearance of significant residual microstresses of the different system-hierarchical levels in the powder microparticles.

(2) It has been shown that, in all cases, the main contribution to an increase in the reactivity of the tungsten powders comes from the change in the enthalpy of the system upon its activation and from the static displacements $\langle U_{\text{st}}^2 \rangle$ of atoms from their sites in the equilibrium crystal lattice. The static displacements stimulate the appearance in the material of local microstresses of the third kind, which increase with increasing time of the mechanoactivation of the powder. The internal stresses of the first and second kind, which are caused by the mechanoactivation of powders, hardly affect the behavior of the corresponding reaction constants. However, the change in the entropy of the system as a result of its mechanoactivation negatively affects the reactivity of the tungsten powder, which is comparable in magnitude with the positive contribution of the internal microstresses of the third kind.

(3) It has been revealed that the greatest effect on the mechanical and reactional properties of powders is exerted upon the mechanoactivation of the surface-oxidized powders; the smallest effect is observed upon the mechanoactivation of the surface-plasticized powders.

ACKNOWLEDGMENTS

We thank V.A. Klyuev and N.N. Loznetsova for assistance in the work.

REFERENCES

1. P. A. Rehbinder, *Surface Effects in Disperse Systems. Physicochemical Mechanics. Selected Papers* (Nauka, Moscow, 1979) [in Russian].
2. V. I. Likhtman, E. D. Shchukin, and P. A. Rehbinder, *Physicochemical Mechanics of Metals* (Akad. Nauk SSSR, Moscow, 1962) [in Russian].
3. E. D. Shchukin, V. I. Savenko, and A. I. Malkin, *Lectures on Physicochemical Mechanics* (Nobel' Press, Moscow, 2015) [in Russian].
4. V. I. Savenko and E. D. Shchukin, "On correlations between phenomenological and structural criteria of working of friction units," *Trenie Iznos* **8**, 581–589 (1987).
5. V. I. Savenko and E. D. Shchukin, "Novel applications of Rehbinder effect," *Trenie Iznos* **13**, 1095–1107 (1992).
6. V. I. Savenko and E. D. Shchukin, "Rehbinder effect simulation at contact interactions," *Materialovedenie*, No. 9, 7–11. (2005).
7. *Fundamental Foundations of Mechanical Activation, Mechanic Synthesis and Mechanicochemical Technologies*, Ed. by E. G. Avakumov, (Sib. Otd. Ross. Akad. Nauk, Novosibirsk, 2009) [in Russian].
8. G. V. Samsonov, A. L. Borisova, and T. G. Zhidkova, *Physicochemical Properties of Oxides* (Metallurgiya, Moscow, 1978) [in Russian].
9. Ch. V. Kopetskii, *Structure and Properties of Refractory Metals* (Metallurgiya, Moscow, 1974) [in Russian].
10. E. B. Leiko and E. M. Nadgornyi, "Peculiarities of mobility of dislocations in single crystals of molybdenum," in *Dynamics of Dislocations* (Naukova Dumka, Kiev, 1975), pp. 53–57 [in Russian].
11. E. B. Leiko, "Study of processes of motion and multiplication of dislocations in single crystals of molybdenum," *Candidate Sci. (Phys.-Math.) Dissertation*, Moscow: MISiS, 1976.
12. E. D. Shchukin and L. A. Kochanova, "Effect of physicochemical factors on the change of the resistance of crystal surface to dislocation motion," in *Dislocation Dynamics* (Fiz.-Tekh. Inst. Nizkikh Temp., Khar'kov, 1968), pp. 520–527 [in Russian].
13. S. S. Gorelik, Yu. A. Skakov, and L. N. Rastorguev, *X-ray and Electronographic Analysis* (Metallurgiya, Moscow, 1994) [in Russian].
14. A. A. Rusakov, *X-ray Diffraction Study of Metals* (Atomizdat, Moscow, 1977) [in Russian].
15. *The Rietveld Method*, Ed. by R. A. Young (Oxford Univ. Press, Oxford, 1995).
16. V. B. Zlokazov and V. V. Chernyshev, "MRIA—A program for a full profile analysis of powder multiphase neutron-diffraction time-of-flight (direct and Fourier) spectra," *J. Appl. Cryst.* **25**, 447–451 (1992).
17. H. Cramér, *Mathematical Methods of Statistics* (Princeton Univ. Press, Princeton, 1946; Mir, Moscow, 1975).
18. P. Scardy and M. Leoni, "Whole powder pattern modeling: Theory and application," in *Diffraction Analysis of Microstructure of Materials*, Ed. by E. I. Mittemeijer and P. Scardy (Springer, Berlin, 2004), pp. 51–91.
19. A. N. Zelikman and L. S. Nikitina, *Tungsten* (Metallurgiya, Moscow, 1975) [in Russian].
20. Yu. P. Toporov, V. I. Savenko, V. A. Klyuev, and A. I. Malkin, "Effect of technological lubricating media on the granulometric characteristics of metallic powders mechanically activated in a ball mill," *Proc. 11th Int. Sci.-Techn. Conf. "Tribology Contribution to Machine Building"* (Inst. Komp'uter. Issledov., Moscow, 2016), pp. 235–236.
21. V. P. Regel', A. I. Slutsker, and E. E. Tomashevskii, *Kinetic Nature of the Strength of Solids* (Nauka, Moscow, 1974) [in Russian].
22. Yu. G. Frolov and V. V. Belik, *Physical Chemistry* (Khimiya, Moscow, 1993) [in Russian].
23. A. I. Malkin, M. P. Kiselev, V. A. Klyuev, N. N. Loznetsova, and Yu. P. Toporov, "The effect of mechanical activation on the heat capacity of powdered tungsten," *Tech. Phys. Lett.* **38**, 509–510 (2012).
24. L. D. Landau and E. M. Lifshits, *Course of Theoretical Physics, Vol. 9: Statistical Physics* (Nauka, Moscow, 1964; Pergamon, Oxford, 1980).

Translated by O. Golosova