

3. The wear resistance of low-hardenability steel 55PP with a hardened layer  $> 0.1$  mm removed by grinding is higher than that of steel 15Kh, and with a layer  $> 0.25$  mm removed it is higher than that of steel 18KhGT.

4. In selecting materials for parts subject to wear in operation, it is necessary to take into account the allowance for machining after heat treatment and if it is  $> 0.2$  mm it is expedient to use low-hardenability steel 55PP subjected to induction hardening.

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#### PHASE AND STRUCTURAL TRANSFORMATIONS DURING HEATING OF MOLYBDENUM CARBIDE COATINGS

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When carbon is saturated with molybdenum the diffusion coating generally consists of hexagonal molybdenum carbide  $\text{Mo}_2\text{C}$ .

In such coatings the orientation of the lattice of grains in the carbide coating changes with increasing thickness, with an increase of the component parallel to the least densely packed direction in the carbide lattice and perpendicular to the surface of molybdenum [1, 2].

Decarburizing of the surface layer adjoining the base metal was observed in studies of the thermal stability of these coatings in a chemically active medium. Microstructural changes were observed in the remaining layer of carbide - dark bands on a light background of carbide.

This work concerns the composition of these layers and the relationship between their arrangement and the formation of metallic phase during decarburization.

A layer of  $\text{Mo}_2\text{C}$  was obtained by carburizing in methane a plate 2-3 mm thick of monocrystalline and polycrystalline molybdenum. The largest surface of the monocrystalline molybdenum was parallel to crystallographic planes  $\{100\}$ ,  $\{110\}$ , or  $\{111\}$ . The samples of polycrystalline molybdenum were grain-oriented with a grain size of  $500 \mu$  and  $< 100 \mu$ , with plane  $\{100\}$  parallel to the surface being saturated. The thickness of the carbide layer on these surfaces was  $30-40 \mu$ . The carbide layers consisted entirely of oriented polycrystalline carbide  $\text{Mo}_2\text{C}$ .

Depending on the crystallographic plane parallel to the surface of the treated plate, the basic orientations observed in the carbide layer were  $(203) \text{Mo}_2\text{C} \parallel (100) \text{Mo}$ ,  $(101) \text{Mo}_2\text{C} \parallel (110) \text{Mo}$ , and  $(114) \text{Mo}_2\text{C} \parallel (111) \text{Mo}$ . On coarse-grained polycrystalline molybdenum, as in the case of single crystals with a surface parallel to crystallographic plane (100), plane (203) of the carbide lattice is parallel to the treated surface, while on fine-grained polycrystalline molybdenum plane (001) was parallel to the surface.

The microstructure of the carbide layers is shown in Fig. 1I.

The formation of metallic phase was investigated after decarburizing of the surface layer of carbide in hydrogen plasma glow discharge with a pressure of 25 mm Hg, combustion potential 600 V, current density  $80 \text{ mA/cm}^2$ .

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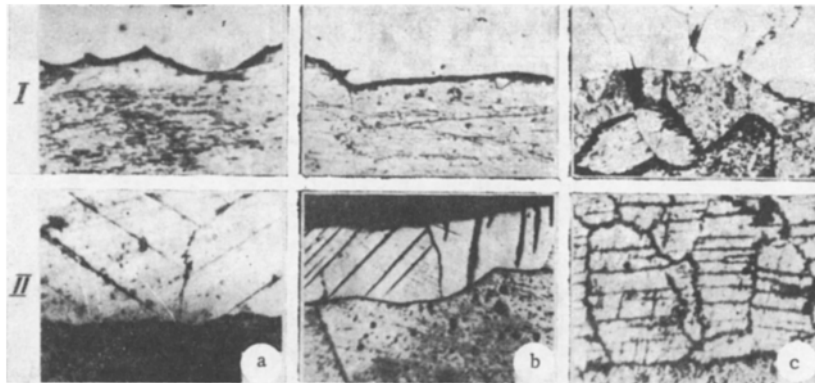


Fig. 1. Microstructure of carbide layers ( $\text{Mo}_2\text{C}$ ) before (I) and after (II) heating.  $300\times$ . a) On monocrystalline molybdenum; b) on polycrystalline molybdenum with a grain size of  $500\ \mu$ ; c) on polycrystalline molybdenum with a grain size of  $100\ \mu$ .

The samples were placed on the cathode of the glow discharge apparatus. The decarburizing time was varied from 20 to 30 min.

Figure 2a shows the microstructure through the cross section of the samples after decarburizing; the linear boundary between the decarburized zone and the remaining layer of carbide is clearly visible; the boundary between the carbide and the molybdenum single crystal has a notable curvature. The microhardness of the decarburized layer of molybdenum is H 270, the lattice constant of this bcc layer is  $3.14 \pm 0.01\ \text{\AA}$  (the thickness of the grains being equal to the thickness of the layer), and it has a perfect texture. Thus, with decarburization of carbide, texture (100) [010] occurs on plane (100) of the molybdenum single crystal in the polycrystalline layer of molybdenum, texture (110) [101] on plane (110), and texture (111) [112] on plane (111). With increasing thickness of the decarburized layer the perfection of the texture decreases.

Thus, with decarburization of molybdenum carbide one observes so-called crystallographic reversibility [3]: The transfer of atoms during the direct process (carburizing of the single crystal) and the reverse process (decarburizing of carbide) along the same diffusion path. Because of this, a peculiar "memory" of the preceding orientation is observed during phase transformation.

To determine the curvature of the boundary between carbide and the molybdenum single crystal we prepared microsections in the plane parallel to the surface of the sample and intersecting the irregular boundary of the carbide (Fig. 2b). It can be seen that the carbide region (lighter in Fig. 2b) has an oval shape, which indicates a globular shape of the carbide protrusions.

It should be noted that in the process of decarburizing the carbide grows into the matrix of the single crystal. This is manifest primarily in the irregularity of the boundary with the monocrystalline metallic phase, i.e., in the development of globules at the carbide phase boundary.

The development of globules on the surface of the growing phase depends in general on impurities accumulating at the carbide-molybdenum boundary [4]. However, the presence of globular protrusions on the surface of the growing carbide may also be due to the direct influence of discharge in the process of decar-

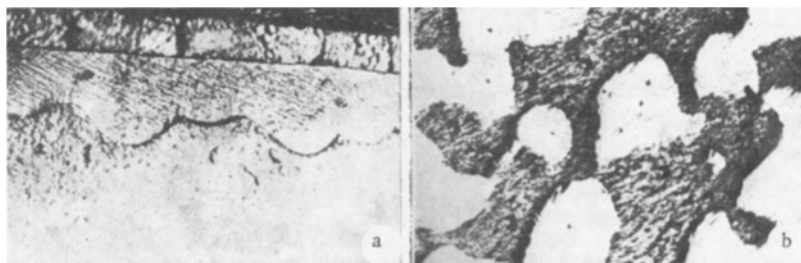


Fig. 2. Microstructure of a sample after decarburization.  $500\times$ . a) In plane perpendicular to the surface of the sample; b) in plane parallel to the surface of the sample and intersecting the boundary between carbide and the molybdenum single crystal.

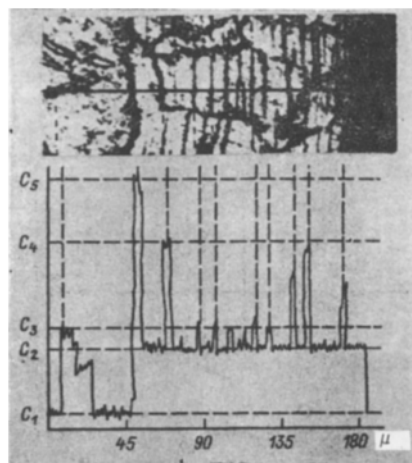


Fig. 3. Distribution of carbon in the carbide layer on molybdenum after heating.  $C_1$ ) In molybdenum;  $C_2$ ) in  $\text{Mo}_2\text{C}$ ;  $C_3$ ) in slip lines;  $C_4$ ) in grain boundaries of  $\text{Mo}_2\text{C}$ ;  $C_5$ ) at the Mo– $\text{Mo}_2\text{C}$  boundary. The lines of the microprobe are shown on the microstructure.

burizing. This effect may be manifest as an uneven density of structural defects in the remaining carbide layer. In connection with this, flow of carbon to the boundary with the molybdenum single crystal may not be constant, which also leads to protrusions whose shape and thickness reflect the uneven flow of carbon.

Structural transformations in the carbide layer during heating were investigated on samples with carbide layers obtained on plane (100) of the single crystal and on texturized samples of polycrystalline molybdenum with (100) texture. Samples with carbide layers were heated in vacuum at  $1800^\circ\text{C}$  for 3 h at a residual pressure of  $10^{-5}$  Hg. Dark bands  $7\text{--}10\ \mu$  wide are distinctly visible in the microstructure of such layers after heating (Fig. 1II). Within the limits of grains or blocks these interlayers are parallel and approximately the same distance from each other.

The x-ray diffraction analysis revealed no new phases in the carbide layers after heating. However, the lattice constants of  $\text{Mo}_2\text{C}$  decreased somewhat after heating ( $a = 3.006\ \text{\AA}$ ,  $c = 4.747\ \text{\AA}$  before heating;  $a = 2.992\ \text{\AA}$ ,  $c = 4.721\ \text{\AA}$  after heating). Microprobe analysis showed that the carbon content of the dark areas is higher than in the light areas (Fig. 3). This leads to the assumption that the reduction of the lattice constants of carbide is due to partial decomposition and accumulation of carbon in certain areas of the layer, leading to formation of the dark interlayers. The ordered distribution of these layers indicates that they are parallel to the crystallographic planes in the carbide lattice. The x-ray diffraction analysis was used to determine the planes in the carbide lattice parallel to the dark interlayers in order to verify this assumption. In all cases this plane, (001), forms one of the slip systems in the lattice of hexagonal carbide  $\text{Mo}_2\text{C}$ . It is not excluded that the redistribution of carbon in the layer during heating is associated with stresses and displacements along slip planes.

The possibility of producing surface carbide layers consisting of alternating layers with different carbon concentrations is of considerable interest, since they serve as diffusion barriers. This property of carbide layers is most effective when interlayers rich in carbon are located parallel to the surface being saturated. The basal plane of the lattice of the carbide layer should be parallel to the surface being saturated. The requirements for the orientation of monocrystalline substrates ensuring the necessary orientation of the lattice of the carbide layer were discussed in [1]. There are no data for polycrystalline substrates. For this reason, we investigated the relationship between the preferred orientation of the lattice of polycrystalline molybdenum and the orientation of the lattice of the carbide formed on it. Primary attention was given to saturation of molybdenum with texture in which plane  $\{100\}$  is parallel to the surface being saturated. This type of texture is most common in bcc metals after rolling and drawing.

The preferred orientation of the carbide lattice was determined after carburizing of molybdenum with a grain size  $\geq 500\ \mu$  and  $< 100\ \mu$ . It was found that the basal plane of the carbide lattice in carbide layers on fine-grained molybdenum is parallel to the surface being saturated. Stratification parallel to the surface of saturation occurs in grains of the carbide layer during heating (Fig. 1IIb). It was impossible to obtain stratification in the required direction in carbide layers on coarse-grained molybdenum (Fig. 1IIb).

The dependence of the direction of stratification on the grain size of the metal being saturated can be explained on the basis of data concerning the saturation of monocrystalline molybdenum [1], where it was found that with small thicknesses of the carbide layer the preferred arrangement of the basal plane is parallel to the surface of saturation. With increasing thickness of the layer the orientation of the carbide lattice changes. With saturation of monocrystalline molybdenum to a depth larger than the average size of the grains the growth of carbide phase in each grain can be considered approximately independent, occurring in the same manner as in monocrystalline molybdenum.

Saturation of molybdenum with large grains leads to orientations of the carbide lattice that are determined by the grain size in the direction of the diffusional flow of carbon. In fine-grained molybdenum the development of such orientations is prevented by the small grain size in the direction of the flow of carbon. Because of this, when the orientation of grains in molybdenum corresponds to texture of the (100) type then because of the small grain size the carbide layer will retain the primary orientation in which the basal planes are parallel to the surface of saturation. In this case the perfection of the orientation obtained depends directly on the grain size of the metal being saturated.

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#### DYNAMICS OF THE PROCESS OF CHANGE IN THE DEGREE OF DISSOCIATION OF AMMONIA IN NITRIDING FURNACES

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The dissociation of ammonia in nitriding furnaces occurs in two stages – heating of ammonia and dissociation by the chemical reaction



Both stages occur with intensive mixing of the gas.

The extent of dissociation  $\alpha$  by reaction (1) depends mainly on the temperature of the process and the ammonia input. Since the temperature depends on the properties of the metal being nitrided, the dissociation of ammonia is controlled in practice by the input [1, 2]. The character of the change in the dissociation of ammonia with time is of interest in this case, i.e., the dynamic characteristic of the furnace. This work was undertaken to determine this characteristic.

Dynamics of Heat Transfer. To determine the heating rate of ammonia one can use the heat balance equation [3], which for a furnace as an ideal mixer [4, 5] in time period  $dt$  takes the form

$$h_1 Q_1 \theta_1 dt + AF(\theta_f - \theta_2) dt - h_2 Q_2 \theta_2 dt = h_2 V d\theta_2, \quad (2)$$

where  $h_1$ ,  $h_2$ ,  $Q_1$ , and  $Q_2$  are the specific heats and the ammonia input and the products of its partial dissociation;  $\theta_1$  and  $\theta_2$  are the initial and final temperatures of the ammonia and its dissociation products;  $\theta_f$  is the furnace temperature;  $V$  is the volume of the furnace;  $A$  is the coefficient of heat transfer from the walls of the retort (muffle) and the surface of the load to the gas;  $F$  is the total contact surface of the load and the walls of the retort.

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