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Modifying Molybdenum Surface with Niobium for Improving the Operational Reliability in the Course of Obtaining Nuclear Fuel

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Abstract

Results are presented concerning the cause of destructing the molybdenum containers those are used in sintering the pellets of fuel uranium dioxide. An effect of niobium ion implantation on changing the microstructure and mechanical properties of molybdenum was studied. It was demonstrated that niobium prevents the formation of carbide, nitride and oxide phases near molybdenum grain boundaries, thereby causing an increase in the operational reliability.

Key words: molybdenum, uranium dioxide, operational reliability, carbides, nitrides, oxides, niobium, nuclear industry

INTRODUCTION

Molybdenum and its alloys are widely used in chemical, aerospace and nuclear industries. The distribution of molybdenum consumption over the regions is characterized by the following data: low-alloy steels 44–45 %, corrosion-resistant steel 21–22 %, tool steel 8–9 %, cast iron 6–7 %, special alloys 3–4 %, products of metallic molybdenum 5–6 %, chemicals 9–10 % [1, 2].

In the nuclear industry, molybdenum is used at the final stages of obtaining nuclear fuel such as a reductive sintering of uranium dioxide pellets. The process takes place in an atmosphere of hydrogen with gradually increasing temperature. The maximum temperature in the furnace amounts to 1750 °C (duration 6 h), whereas the total cycle time is equal to 36 h. Such severe conditions can be withstood only by molybdenum, that is a material for making furnace mountings and containers wherein the

uranium dioxide pellets are to put. Molybdenum, used for making containers by means of a powder metallurgy method, contains the following impurities, mass %: C 0.004, Na 0.003, Ca 0.008, Al 0.004, Fe 0.01, Ni 0.005, W 0.013.

Using the molybdenum at high temperature values in a hydrogen atmosphere results in worsening the strength characteristics. Under these conditions, the plasticity of the material decreases to a considerable extent, whereas the microhardness demonstrates an insignificant increase. On the metal surface there are cracks occurring, to result in changing the geometrical shape by the containers, in the contamination of the molybdenum surface by uranium oxide, aluminium oxide, by the compounds of K, Ca, Si, Fe, C, N. The presence of aluminium, silicon, nitrogen and carbon within the surface layer of the metal could be explained by the fact that the formation of uranium oxides fuel pellets is performed with using such

TABLE 1

Mechanical characteristics of intact molybdenum and that of molybdenum after performing the operation cycles

Number of cycles	Vickers micro-hardness, MPa	Young's modulus, GPa
0	293	46
19	316	230
50	379	244
100	375	243

plasticizer as distearylethylenediamine ($C_{38}H_{76}O_2N_2$) and the additions of Al_2O_3 , SiO_2 .

Table 1 demonstrates the results concerning the mechanical parameters for intact molybdenum containers and containers subjected to 19, 50 and 100 operation cycles. The mechanical properties of molybdenum were determined using CSM indentation unit. As the indenter, we used a diamond pyramid which was pressed into the metal with a load amounting to 300 mN.

Figure 1 demonstrates the microstructure of the surface of molybdenum containers after the operation. Determining the structure and local elemental analysis were performed using a Philips SEM 515 electron microscope and EDAX ECON IV electron probe microanalyzer.

The main cause determining the destruction of molybdenum consists in a grain-boundary diffusion of the gaseous compounds of nitrogen and carbon resulting from the atmosphere of the furnace, which gives rise to the formation of molybdenum carbides and nitrides on the surface of the grain boundaries [3, 4].

The duration of operation with molybdenum containers ranges within 40–60 cycles; thereafter the containers are taken out of production to store at the enterprises of nuclear industry. The destruction of a container in the course of the production of uranium dioxide can cause damaging the furnace as well as its contamination by uranium. Increasing the operation reliability of the containers would allow reducing the amount of anew formed radioactive molybdenum wastes, improving the reliability of furnace operation as well as reducing the costs of nuclear fuel production.

In order to modify the surface of metals one uses different types of chemical, thermal and mechanical treatment [5]. Of wide application

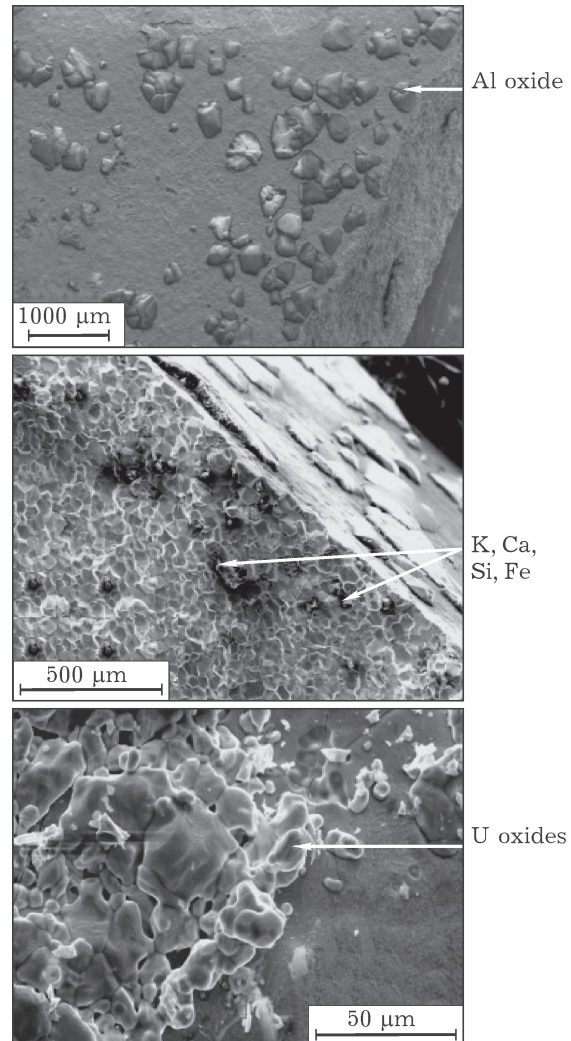


Fig. 1. Micrographs of molybdenum surface after operation.

for these purposes are high-energy impact methods such as laser, plasma, ion-plasma and others [6]. Remarkable results in the hardening of the materials were obtained with processing the surface by the beams of relativistic electrons and the high-power beams of charged particles [7]. However, the mentioned methods are complicated and require, as a rule, for expensive equipment and highly skilled personnel.

One of the ways to increase durable molybdenum strength consists in modifying the molybdenum surface by a refractory metal or an alloy which should be inert with respect to uranium dioxide under sintering and should exhibit a low value of the thermal neutron capture cross section. For this purpose, it is promising to use niobium. It is known [8–10] that

vanadium, niobium, tantalum, titanium and zirconium are used as alloying elements in order to increase the level of heat resistance, viscosity and strength of many structural and heat-resistant alloys. The introduction of the above mentioned alloying elements promotes the formation of fine-grained structure, and since the operation with molybdenum is performed at high temperature values, it is assumed that the thermal treatment and concomitant diffusion saturation of the surface molybdenum layers by niobium could take place directly in the course of the operational cycle.

EXPERIMENTAL

The coating was applied using a laboratory set-up (Fig. 2) with the help of a gas transport method according to the reaction



In order to modify the molybdenum surface we used analytical grade niobium powder, analytical grade crystalline iodine, and high purity grade argon. As a substrate material, we used molybdenum plate, 20 × 20 × 2 mm in size with the content of the main element equal to 99.95 mass %.

The set-up consisted of a horizontal quartz reactor 3, 1 m long and 0.03 m in diameter, with two heating zones, and electrical devices for measuring the temperature. As a carrier gas, we used argon purified from oxygen in a column with a pyrogallol. Iodine was supplied from the evaporator 2.

The plate of molybdenum was weighed and placed into the right side of the quartz reactor 3. A weighed portion of niobium powder, 0.5 g,

was loaded into the left side of the reactor 3. The crystalline iodine was placed into the evaporator 2 and then the communications between the elements of the laboratory set-up were hermetically connected.

After purging the system, the argon gas flow rate was maintained to be equal to 1 L/min. The temperature in the zone of fusion (left side) was equal to 770–800 °C, whereas the temperature in the zone of niobium iodide decomposition on molybdenum (right side) amounted to 1150–1200 °C. The air thermostat was heated up to 110 °C, the partial pressure of iodine at this temperature amount up to 20 kPa. The experiment was carried out for 4 h. After the experiment was completed, cut the electric heater of the thermostat, and that of the reactor were switched off. The sample of molybdenum was cooled in a flow of argon up to 50–70 °C and the flow of argon was then cut off.

The samples of molybdenum modified with niobium, as well as the initial molybdenum plates were tested at the Novosibirsk Chemical Concentrates Plant OJSC. The molybdenum samples were placed into molybdenum containers with the pellets of uranium dioxide to perform testing in an industrial furnace for the reductive sintering of uranium dioxide pellets during 720 h (20 operation cycles).

After the testing, a comparative analysis of the microstructure of molybdenum samples was performed using a Philips SEM 515 scanning electron microscope, the phase composition was studied by means of a Shimadzu XRD 6000 X-ray diffractometer, the microhardness and Young's modulus were measured with the help of CSM indentation unit (as an indenter,

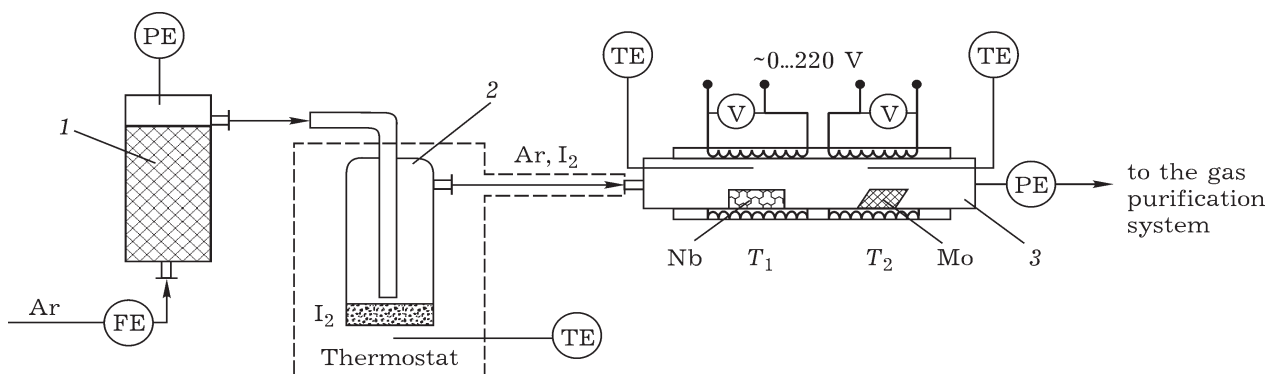


Fig. 2. Schematic diagram of laboratory setup for molybdenum surface modifying with niobium: 1 – column for purifying argon from oxygen, 2 – iodine evaporator, 3 – reactor for gas-transport applying the niobium coating.

we used a diamond pyramid, which was pressed into the metal with a load equal to 300 mN).

RESULTS AND DISCUSSION

Figure 3 demonstrates the micrographs of the initial and niobium-modified molybdenum plates after 720 h of testing test in the furnace for the reductive sintering of uranium dioxide.

It was established that the microstructure of the surface of molybdenum plates is markedly different from the microstructure of the bulk sample. Testing in the reductive sintering furnace resulted in molybdenum recrystallization and grain growth. From a deformed structure [4], equiaxed grains were observed to form. In the surface layer of molybdenum (see Fig. 3, *a*) there are a large number of channels observed, located mainly on grain boundaries, where trough an intergranular diffusion of oxygen, nitrogen and carbon into the bulk metal occurs, resulting in the formation of molybdenum carbides and nitrides at the grain boundaries. The

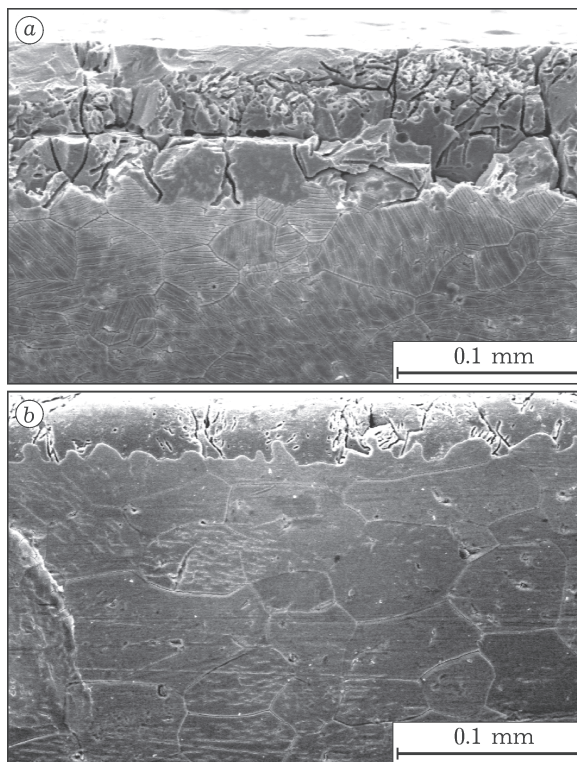


Fig. 3. Micrographs of the butt surface of molybdenum after 720 h of testing: *a* – intact niobium sample, *b* – sample modified with niobium.

presence of molybdenum carbides and nitrides on the metal surface was confirmed by X-ray diffraction phase analysis.

Figure 4 demonstrates a diffraction pattern of the initial molybdenum plate (internal volume and surface) after 720 h of testing. The average content of molybdenum carbide and nitride within the surface layer is: Mo₂C trigonal modification ($a = 0.5090$, $c = 0.4732$ nm) 12 vol. %, Mo₂C orthorhombic modification ($a = 0.4745$, $b = 0.6012$, $c = 0.5304$ nm) 8 vol. %, Mo₂N tetragonal modification ($a = 0.4295$, $c = 0.7900$ nm) 7.5 vol. %. At the depth of 0.2 mm from the surface, molybdenum carbide and nitride were not found.

Figure 5 demonstrates a diffraction pattern of the molybdenum surface modified with niobium, after the testing. The surface layer contains up to 1 vol. % of Nb, representing a substitutional solid solution in molybdenum, up to 1 vol. % of Mo ($a = 0.3146$ nm), up to 58 vol. % of MoO₃ ($a = 0.713$, $b = 0.537$, $c = 0.557$ nm), 20 vol. % of Mo₂N

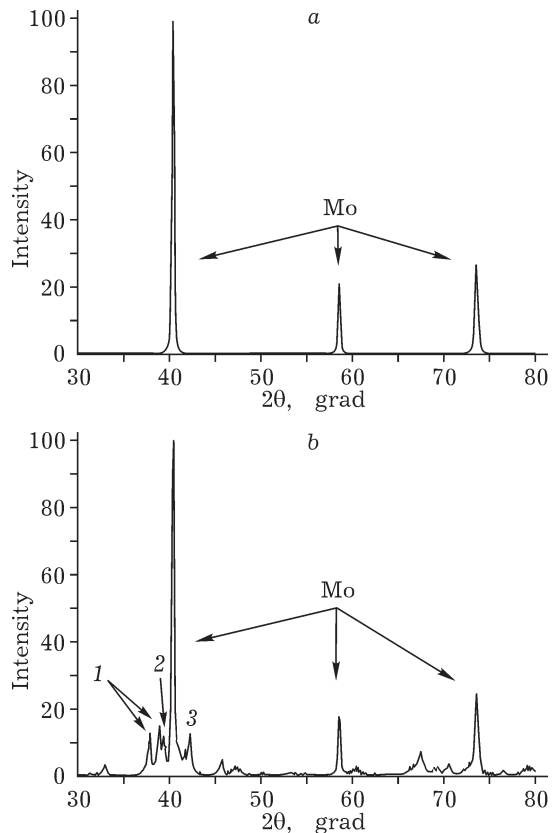


Fig. 4. X-ray diffraction patterns for intact molybdenum after 720 h of testing: *a* – bulk, and *b* – surface layer: 1–3 – Mo₂C trigonal, Mo₂C orthorhombic and Mo₂N tetragonal modifications, respectively.

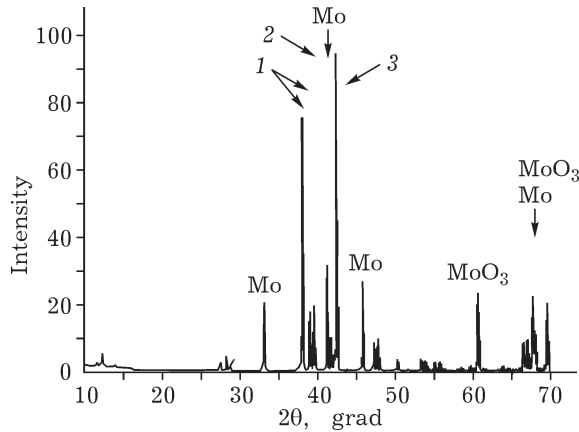


Fig. 5. X-ray diffraction patterns of the surface of niobium-modified molybdenum, after 720 h of testing: 1–3 – Mo_2C trigonal, Mo_2C orthorhombic and Mo_2N tetragonal, respectively.

($a = 0.4295$, $c = 0.7900$ nm), 20 vol. % of Mo_2C ($a = 0.4745$, $b = 0.6012$, $c = 0.5304$ nm).

According to the analysis of micrographs for intact (initial) and modified molybdenum samples, the thickness of the defect layer for niobium-modified molybdenum (see Fig. 3, b), is three times less than that for the initial molybdenum (see Fig. 3, a): 0.03 and 0.1 mm, respectively. In addition, the niobium-modified molybdenum is characterized by a smaller number of defects in the structure of the surface layer.

For niobium-modified molybdenum samples, after 720 h of testing there is a relatively low value of Young's modulus (147 GPa) observed, with a more than three times increased microhardness (1437 MPa), comparing to the initial sample exhibiting these parameters to be 161 GPa and 423 MPa, respectively. This fact indicates that there is an efficient surface hardening, whereas the ability with respect to plastic deformation decreases into a considerable extent.

Molybdenum which is used in the nuclear industry in the course of the sintering of energy fuel from uranium dioxide represents a polycrystalline metal. The presence of the developed system of internal interfaces (grain boundaries, subgrains and secondary phases) determines in many respects its physicochemical, mechanical, electrical and other properties. Grain boundary processes controlled by diffusion, play an important or even a decisive role in the development of plastic deformation, degradation and destruction of the structure

of metal polycrystals. Under such conditions, the plastic forming is realized *via* a joint action of different mechanisms such as dislocation gliding, diffusion mass transfer and friction along the grain boundaries and moving the grains as a whole [9, 10].

The effect of the diffusion fluxes from the external environment (hydrogen which is used as a reducing agent for uranium oxides, nitrogen and carbon gaseous compounds those were formed in the course of thermal decomposition of ligament materials, water vapour which is added in small amounts to the reducing atmosphere of the furnace, oxygen released from uranium oxides) is expressed in changing the status of molybdenum thin surface layers. The latter, in turn, exert a significant effect on the development of deformation and fracture processes at the macroscopic level. The changes in the structure of the surface layers are clearly visible for all the samples after 720 h of testing (see Fig. 3).

The diffusion of impurity atoms along the grain boundaries from the surface layers into the metal bulk results in a significant reduction in the operational reliability due to premature destruction of the grain boundaries. This phenomenon indicating the occurrence of metal embrittlement was also found for a number of polycrystalline metals [4].

The positive influence of niobium upon the mechanical properties of molybdenum in the surface modification is determined by a successful combination of its properties. Niobium exhibits satisfactory strength, high temperature strength, ductility, high corrosion resistance in different chemical environments, high melting temperature, low temperature interval of ductile-to-brittle transition, almost the same coefficient of linear expansion, low thermal neutron capture cross section and an inertness with respect to uranium dioxide. Due to the same type and approximately the same parameters of crystal lattices, molybdenum and niobium can form a substitutional solid solution with the unlimited solubility of components.

Niobium is characterized by a slightly higher limit of solubility and chemical reactivity with respect to oxygen, nitrogen and carbon as compared to molybdenum [9, 10]. As the result, niobium-modified molybdenum in the course of operation at elevated temperatures

would interact with the atmosphere of the furnace to dissolve a few more carbon, nitrogen and oxygen, with preventing the formation of supersaturated solid solutions, as well as with forming the dispersed particles of niobium and molybdenum carbides, nitrides and oxides. In this case niobium carbides and nitrides are more stable comparing to molybdenum carbides and nitrides; they exhibit higher hardness, strength and melting point.

The effect of molybdenum dispersion hardening with the use of chemical and thermal treatment methods resulting in an increase in the heat resistance, long-term strength limit as well as in decreasing the limit of the brittle-ductile transition was mentioned in many papers, too. So, molybdenum could be strengthened by titanium, zirconium, hafnium, niobium, tantalum, tungsten, rhenium carbides as well as by zirconium, hafnium oxides, titanium nitrides [9, 10].

It was also found that the trace amounts of niobium prevent the grain size from increasing in the course of recrystallization, which also reduces the tendency to brittle fracture inherent in molybdenum.

Thus, modifying the surface of molybdenum with niobium results in the formation of a substitutional solid solution which serves as an efficient diffusion barrier preventing the interstitial phases from segregation along the grain boundaries of molybdenum and reducing the amount of internal defects in the structure and the embrittlement. The interpolation of the basic strength characteristics demonstrated that there is a possible increase in the operation lifetime of niobium-modified molybdenum up to 40–60 %.

CONCLUSION

Using the method of gas-transport reactions, molybdenum surface was modified with niobium and the samples were tested under the conditions of uranium dioxide reductive sintering.

According to X-ray diffraction patterns for molybdenum after testing, the surface composition of molybdenum differs to a considerable extent from that in the bulk sample. The presence of different Mo_2C and Mo_2N modifications is inherent in the molybdenum surface, whereas in the bulk of the sample (at the depth of 0.2 mm) there are no such phases detected.

It was established that niobium causes a diffusion barrier to occur on the surface of molybdenum, which improves the operational reliability of the metal.

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