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Effect of High-Dose Ion Implantation of Niobium on Changing the Mechanical Properties and Structure of Molybdenum Used at the Stage of Sintering Nuclear Fuel from Uranium Dioxide

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Abstract

Results of the investigation of reasons causing the destruction of molybdenum containers used for sintering the pellets of fuel uranium dioxide are reported. An effect of niobium ion implantation changing the microstructure and mechanical properties of molybdenum was investigated. It was demonstrated that niobium prevents the formation of carbide, nitride and oxide phases on the boundaries of molybdenum grains, causes the rate of metal grain growth in the course of recrystallization to decrease and stabilizes mechanical properties thus increasing the operational reliability by 30–60 %.

Key words: molybdenum, uranium dioxide, destruction, molybdenum carbides, molybdenum nitrides, molybdenum microstructure, ion implantation, operational reliability

INTRODUCTION

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

In the nuclear industry, molybdenum is used at the final stage of producing nuclear fuel, i. e. for reductive sintering uranium dioxide pellets. The process proceeds in a hydrogen atmosphere at a gradually increasing temperature. The maximum temperature in the furnace is equal to 1750 °C (the process duration being of 6 h), whereas the total cycle duration time amounts to 36 h. Such severe conditions can be withstood only by molybdenum that is used for making furnaces and containers, wherein uranium dioxide pellets is placed. The molybdenum that is used for making containers by means of powder metallurgy technique followed by rolling procedure 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.

Operation with molybdenum at high temperature values in an atmosphere of hydrogen results in the loss of operational reliability. Cracks appear on the metal surface, the geometric shape of the container changes, to cause the pollution of molybdenum surface by uranium oxides, aluminium oxide, and compounds K, Ca, Si, Fe.

Table 1 demonstrates the mechanical characteristics for original molybdenum containers, and containers after 19, 50 and 100 operation cycles.

Figure 1 demonstrates the microstructure of molybdenum containers after use.

The main causes of molybdenum destruction are they: grain boundary diffusion of gaseous nitrogen and carbon compounds appeared from the furnace atmosphere, which results in the formation of molybdenum carbides and nitrides on the surface of the grain boundaries, as well in increasing the grain size due to recrystallization; in addition, hydrogen embrittlement is observed [3, 4].

The operating time duration for molybdenum containers amounts to 40–60 cycles, after which they are taken out of production to store at the enterprises of the nuclear industry. The destruction of a container in the course of producing uranium dioxide could cause damaging the furnace to result in uranium contamination. Improving the operational reliability of containers should reduce the amount of newly formed radioactive molybdenum wastes with improving the reliability of the furnace and reducing the cost of manufacturing the nuclear fuel.

Extensive potentialities of controlled modifying the chemical composition, structure and properties of ultrathin (10–100 μm) surface layers are offered by the method of ion implantation. With the help of the mentioned method, one could produce in the surface layers the alloys with such a composition that can not be obtained in any other way. The ion implantation results in the formation of phases those are difficult to describe by the equilibrium phase diagram. Owing to the combination of a high supersaturation level of solid solution, the dispersion, structural and substructural hardening, one could significantly increase the strength, wear and corrosion resistance, with providing the long-term strength of structural and heat-resistant metals and alloys [5–8].

One of the ways to increase the operational reliability level of molybdenum consists in modifying the surface with a refractory metal or alloy that is inert with respect to the uranium dioxide under sintering and exhibits a low capture cross section with respect to thermal neutrons. For this purpose it is prospectively to use niobium. It is known [5, 6] that vanadium, niobium, tantalum, titanium and zirconium are used as alloying constituent elements in order to increase the heat resistance, toughness and strength of many structural and heat-resistant alloys.

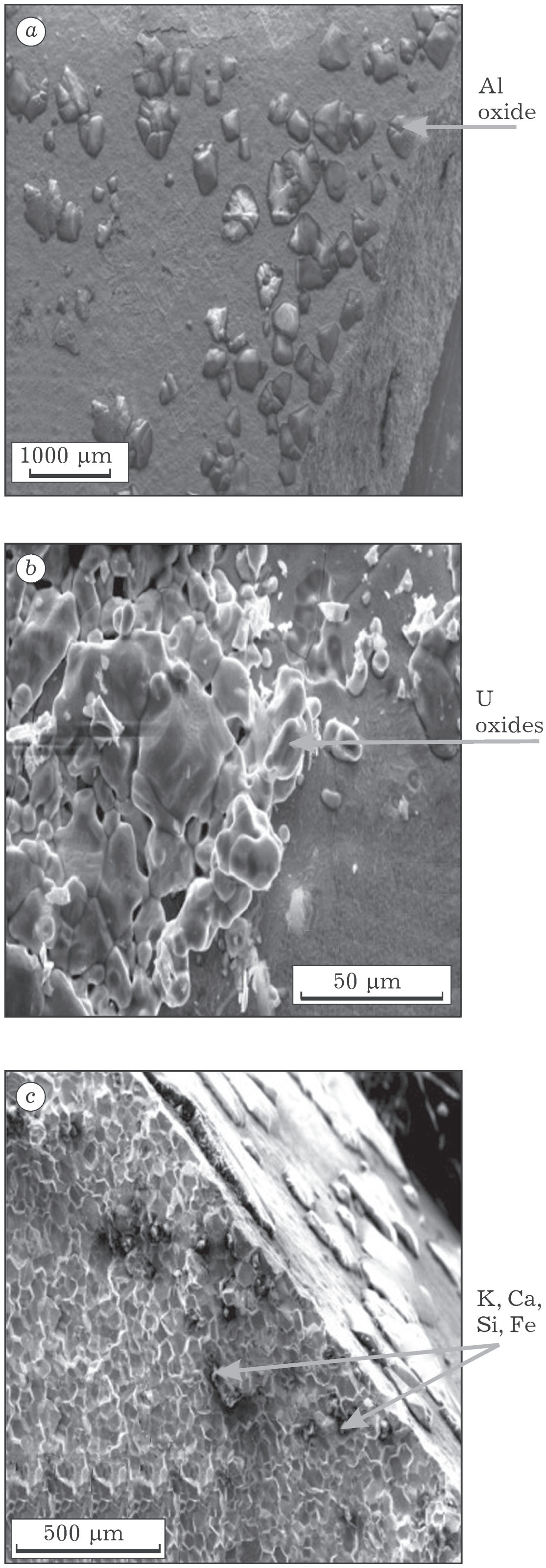

Fig. 1. Photomicrographs of molybdenum surface after operation: *a* – outer surface of container, *b* – inner surface of container, *c* – end surface of a break.

TABLE 1

Microhardness and Young's modulus (E) for the original molybdenum, and molybdenum after the operation

Number of operation cycles	Vickers microhardness (VH)	Microhardness (E), GPa
0	293	46
19	316	230
50	379	244
100	375	243

Thus, in order to improve the reliability of the power-plant fuel production area and to reduce the amount of the newly formed radioactive wastes it is necessary to develop a technology for improving the operational reliability of molybdenum containers used at the stage of uranium dioxide reductive sintering.

EXPERIMENTAL

In order to modify the surface, molybdenum via the ion implantation of niobium we used a Diana-3 technological accelerator (Fig. 2). This ion source is the most promising for the treatment of metallic structural materials, where high doses of radiation with medium energy are required. Source allows one generate ion beams with a high ion current density and can provide a multiple, high-dose, high-concentrated and other implantation modes. The accelerator operated in a pulse frequency mode, the accelerating voltage 60 kV, pulse repetition rate being of 50 Hz, with 200 μs duration, the pulse ion current strength amounting up to 300 mA, fluence 10^{17} ions/cm^2. The diameter of the ion beam spot on the target was equal to 0.3 m. The implantation was performed with niobium ions.

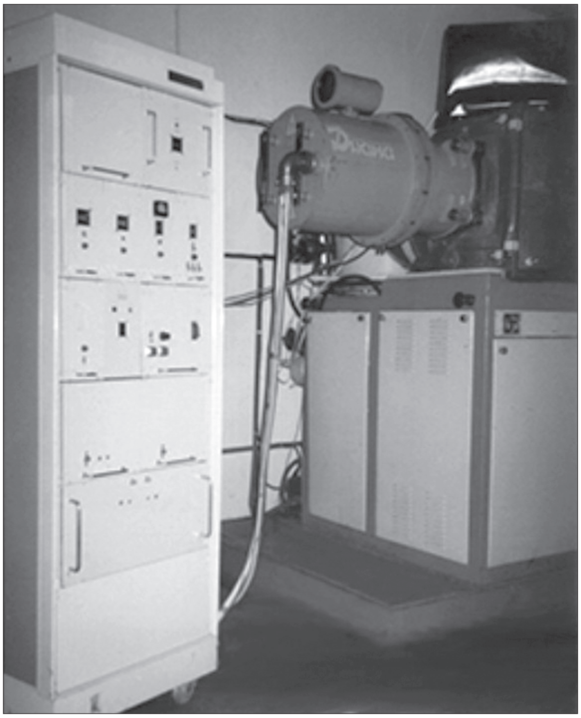

Fig. 2. Diana-3 technological implanter located on the vacuum chamber.

As the targets for niobium ion implantation we used the elements of a molybdenum container (boat), of rectangular and cylindrical shape, those were placed into a VU1-B vacuum chamber. The surface modification was performed on both sides.

The temperature of the samples under processing did not exceed 150 °C.

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

After the testing, we performed a comparative analysis of the microstructure molybdenum samples using a Philips SEM 515 scanning electron microscope. The phase composition was investigated using a Shimadzu XRD 6000 X-ray diffractometer, the micro-hardness value and Young's modulus were measured with a CSM indentation unit. As an indenter we used a diamond pyramid, which was pressed into the metal with a load equal to 300 mN.

RESULTS AND DISCUSSION

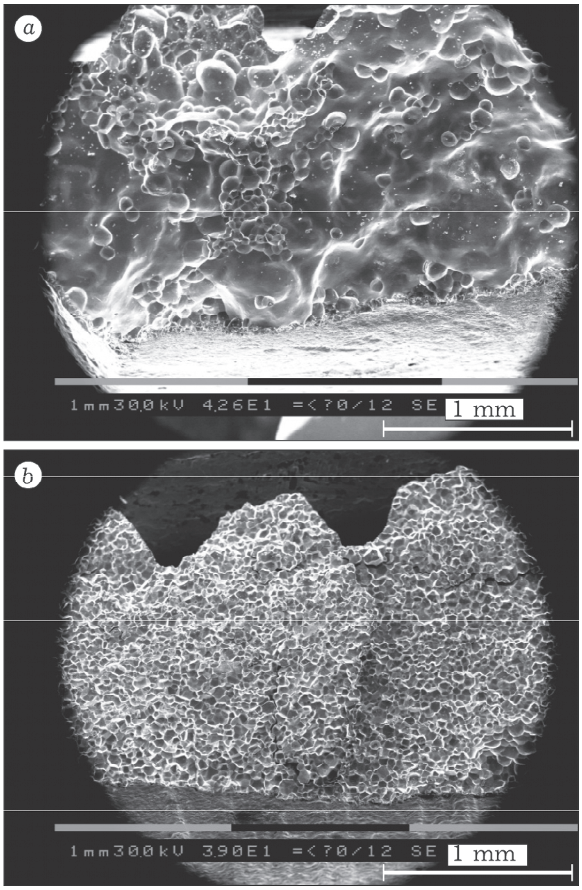

Fig. 3. Microstructure of break surface for the samples of unmodified (*a*) and niobium-modified (*b*) molybdenum, after 720 h of testing.

Figure 3 demonstrates the microstructure of unmodified molybdenum and molybdenum modified with niobium after 720 h of testing in the furnace for the reductive sintering of uranium dioxide.

The testing resulted in molybdenum recrystallization and grain growth. Basing on the deformed structure [4], equiaxed grains were formed. The microstructure features of the molybdenum samples modified and unmodified with niobium exhibit a fundamental difference: the former are characterized by a coarse-grained structure, where the linear grain size ranges from 50 μm to 1 mm, whereas the latter represents a uniform fine-grained structure throughout all the volume with an average grain size within the range of 30–60 μm.

In the surface layer of the samples of niobium-modified and unmodified molybdenum, there is a great number of channels observed, preferably located on the grain boundaries along those the intergranular diffusion of oxygen, nitrogen and carbon to the bulk of the metal occurs. As the result, molybdenum carbides and nitrides are formed on the grain boundaries. Their presence on the metal surface is confirmed by means of X-ray diffraction analysis. Figure 4, *a* demonstrates an XRD profile of molybdenum surface layer modified with niobium, after 720 h of testing, whereas Fig. 4, *b*, *c* present the XRD profiles of internal layers for unmodified and modified molybdenum samples

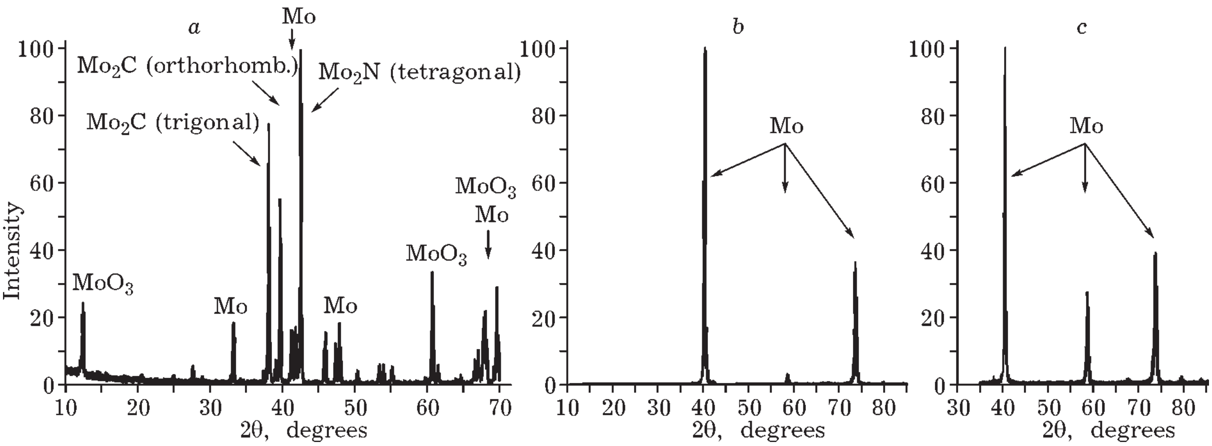

Fig. 4. X-ray diffraction patterns of the surface layer for molybdenum sample modified with niobium (*a*), internal layers of unmodified samples (*b*) and molybdenum modified with niobium and (*c*) after 720 h of testing.

TABLE 2

Microhardness and Young's modulus (E) for the surface and internal layers of molybdenum samples modified and unmodified with niobium, after 720 h of testing

Molybdenum samples	Vickers microhardness (VH), kgf/mm^2	Microhardness, GPa	E, GPa
Unmodified molybdenum (surface layer)	1102	11.677	103
Modified molybdenum (surface layer)	718	7.612	47
Unmodified molybdenum (internal layer)	285	3.028	256
Modified molybdenum (internal layer)	216	2.287	80

after the testing. The surface layer of the sample (see Fig. 4, *a*) contains molybdenum trioxide (55–60 %), molybdenum carbide (30–35 %), molybdenum nitride (5–10 %), the rest being molybdenum. The chemical composition of internal molybdenum layers unmodified and modified with niobium ions is the same (see Fig. 4, *b*, *c*).

Table 2 demonstrates the results of measuring the microhardness and the Young's modulus for the surface and internal layers of molybdenum samples unmodified and modified with niobium after 720 h of testing.

According to the results of studying the mechanical characteristics of the molybdenum samples whose surface is modified niobium ions, there is a significant reduction in Young's modulus and microhardness observed. In this case the mechanical properties of molybdenum samples (see Table 2) are comparable with those inherent in the material of the molybdenum containers before the operation (VH = 290 kgf/mm^2, E = 46 GPa [4]).

Molybdenum which is used in the nuclear power industry for sintering uranium dioxide fuel represents a polycrystalline metal. The developed system of internal interfaces (grain boundaries, sub-grains and secondary phases) determines to a considerable extent his physicochemical, mechanical, electrical and other properties. The grain-boundary diffusion controlled processes play an important or even a decisive role in the development of plastic deformation, structural degradation and destruction of metallic polycrystals. Under such conditions, the plastic deformation is realized via the joint action of the different mechanisms: dislocation slip, diffusion mass transfer, sliding along grain boundaries and grain movement as a whole [5].

The impact of diffusion fluxes from the external environment (hydrogen used as a reducing agent for uranium oxides, gaseous compounds of nitrogen and carbon, those are formed in the course of the thermal decomposition of binder materials, the vapour of water that is added in a small amount to the reducing atmosphere of the furnace, the oxygen released from the uranium oxide) causes changing the state of the thin molybdenum surface layers, which, in turn, exerts a significant influence upon the development of the processes of deformation and fracture at the macro level. Changing the structure of the surface layers is distinctly observed for all the samples after 720 h of testing (see Fig. 3), as compared with the original deformed structure [4].

The diffusion of impurity atoms at the grain boundaries of the surface layers in the bulk of the metal results in a significant reduction of the operational reliability value due to premature destruction at the grain boundaries. This phenomenon that determines hard metal brittleness was also observed for a number of polycrystalline metals [5].

The presence of niobium in trace amounts within the surface layer allows one to reduce the rate of grain growth, to reduce the number of internal structural defects and the depth of the degraded surface layer of molybdenum as well as to reduce the brittleness. As the result of testing the samples at the NCCP it was found that the service life of molybdenum modified by niobium used in the course of reductive sintering the uranium dioxide exhibits a 30–60 % increases.

CONCLUSION

The surface of molybdenum was modified by means of niobium ion implantation, the samples obtained were tested under industrial conditions in the furnace for reduction sintering the fuel uranium dioxide.

According to XRD patterns of molybdenum after the testing, the composition of molybdenum on the surface significantly differs from the composition in the bulk of the sample. So, the presence of various Mo_2C and Mo_2N modifications is inherent in the surface, whereas in the bulk of molybdenum sample (0.3 mm in depth) these phases were not detected.

The presence of niobium trace amounts in molybdenum results in reducing the surface defect layer, in decreasing the rate of grain growth, in a considerable decrease of the amount of internal structure defects, of interstitial alloy phases and, as a result, in reducing the brittleness of the metal. The studies demonstrated that the operation life of molybdenum modified by niobium used in the reductive sintering of uranium dioxide demonstrates a 30–60 % increase.

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