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PROTECTION OF MOLYBDENUM CONTAINERS USED AT URANIUM DIOXIDE SINTERING FROM GRAIN BOUNDARY DIFFUSION OF OXYGEN AND NITROGEN

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The results of investigating the reasons of damaging molybdenum containers used at energy tablets sintering from uranium dioxide have been given. The influence of niobium protective coating on changing molybdenum microstructure and properties is investigated. It is shown that protective coating prevents the formation of carbide, nitride and oxide phases on the boundary of molybdenum grains increasing thereby the durability.

Introduction

Molybdenum enters into the group of refractory metals with cubic volume-centered lattice (V, Nb, Ta, Cr, Mo, W) being one of the most important industrial metals.

Physicochemical, mechanical and technological properties of molybdenum depend to a large degree on content of interstitial impurities in it: oxygen, hydrogen, nitrogen and carbon as well as on grain size, distribution and form of impurity inclusion extraction.

Due to the good combination of valued physicochemical and mechanical properties molybdenum and alloys on its basis are widely used in chemical, aircraft, rocket and nuclear industry [1].

Manufacturing tablets of energy uranium dioxide the molybdenum containers are used at the final stage of their sintering in the furnaces in reducing atmosphere. Decrease of plasticity, strength occurs at maintaining; the surface is contaminated with uranium oxides. As a result molybdenum containers become unusable for further use; they are taken out of production and stored at enterprises of nuclear industry.

Due to the high cost of molybdenum on Russian market it is necessary to solve the task of increasing molybdenum containers durability.

The main reason of molybdenum container damage is the grain boundary diffusion of nitrogen and carbon gaseous compounds from furnace atmosphere resulting in formation of molybdenum carbide and nitride on the surface of grain boundary causing hard-metallic fragility [2].

One of the main ways of increasing molybdenum container durability is the protection of molybdenum surface with the film from refractory metal or alloy which would be inert to the sintered uranium dioxide and would probably have low section of thermal neutron capture. The perspective protecting element is niobium. It is known [3–5] that vanadium, niobium and tantalum are used as alloying elements for increasing heat resistance, viscosity and strength of many constructional and heat-resistant alloys.

Experimental technique

To cover protecting niobium film on molybdenum surface niobium powder of «AR» qualification, crystal iodine «AR», argon «AR» were used. Molybdenum plate with the sizes of 20×20×2 mm with the main element content of 99,9 wt. % was taken as the base material. Covering was carried out by gas-transport technique according to the reaction $Nb+I_2 \leftrightarrow NbI_5$ at the laboratory device, Fig. 1.

The device represents a horizontal quartz reactor – 3 with the length of 1m and diameter of 0,03 m with two sections of electric heating and devices for measuring section temperature. The device is equipped with a unit of batching and refining gas from oxygen and water vapors. It consists of a bulb with argon and a column – 1, filled up with pyrogallol. Iodine was fed from the evaporator – 2, placed in thermostat.

The molybdenum plate was weighed, measured and then placed to the right part of quartz reactor – 3. The batch from niobium powder in the amount of 0, 5g was

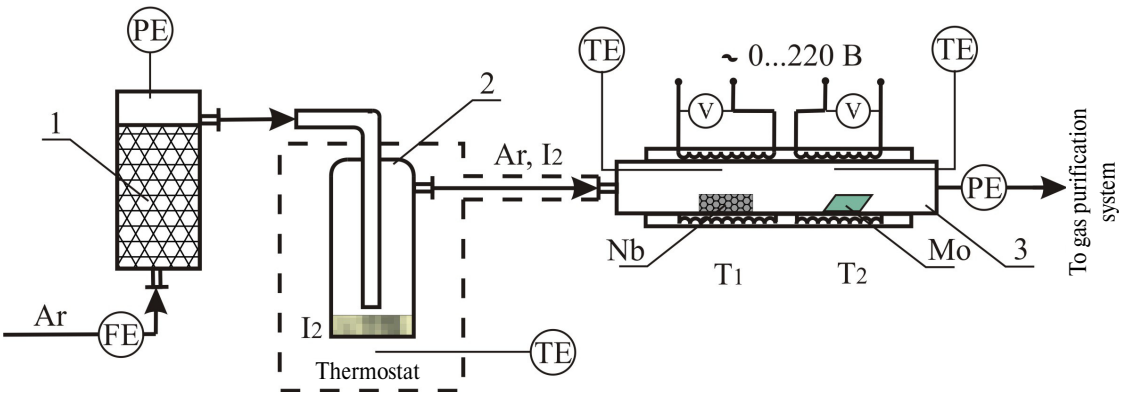

Fig. 1. *Diagram of the laboratory device for covering niobium coating on molybdenum by gas-transport technique: 1) column of argon refining from water and oxygen vapors; 2) iodine evaporator; 3) reactor of gas-transport covering of niobium coating*

placed in its turn to the left part of the reactor. After that crystal iodine was placed into the evaporator – 2 and communications between the elements of the laboratory device were hermetically connected.

After blowing the system with argon the consumption of the latter was determined equal to 1 l/min; the left part of horizontal reactor was heated up to 800 °C and the right one was heated up to 1200 °C. Then thermostat was heated to the temperature 110 °C in this case iodine partial pressure amounted to 20 kPa. At the expiration of the assigned period of time the evaporator – 2, horizontal reactor – 3 were cooled and only achieving the temperature in the reactor 50...70 °C argon supply was switched off.

Then molybdenum plates covered with niobium and initial molybdenum plates were delivered to «NZHK» where they were placed into molybdenum containers together with tablets from uranium dioxide and transmitted through sintering furnace UO_2. The process of uranium dioxide sintering occurs in hydrogen atmosphere with gradually rising temperature. The maximal temperature in the furnace amounts to 1750 °C (period duration is 5...6 h) and total cycle duration is 36 h.

After 20 sintering cycles the comparative analysis of microstructure was carried out using scanning electron microscope Philips SEM 515; the comparative analysis of phase composition was carried out at roentgen diffractometer Shimadzu XRD 6000.

Experimental results

Micrographs of the initial molybdenum plates and the plate covered with niobium film after 20 sintering cycles are presented in Fig. 2.

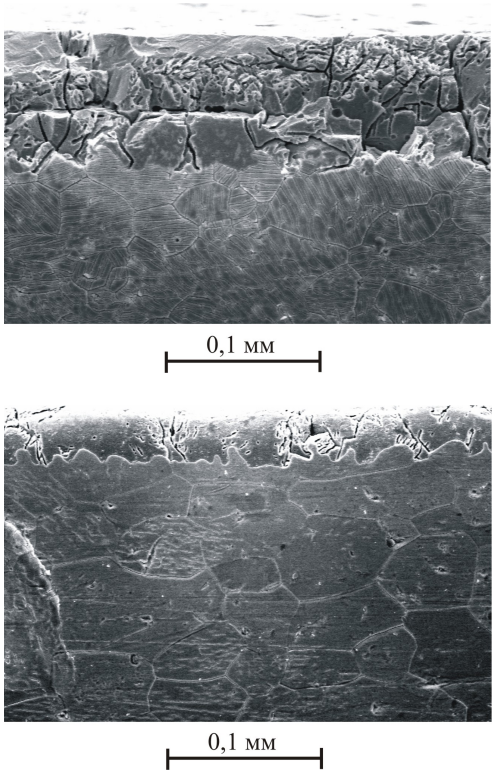

Fig. 2. *Micrograph of the end surface of molybdenum plate sample: a) initial; b) with niobium protecting film*

It is seen from the Figure that microstructure of molybdenum plate exterior differs considerably from the interior. As the samples pass thermal cycles in sintering furnace of uranium dioxide the molybdenum was recrystallized and the grain grew. The outer surface of the plates is covered with a large quantity of channels mainly set on grain boundaries along which intercrystalline diffusion of gaseous compounds of nitrogen and hydrogen resulting in formation of molybdenum carbides and nitrides on grain surfaces occurs. Presence of molybdenum carbides and nitrides on molybdenum plate surface is proved by the results of roentgenophase analysis. The diffraction patterns of the initial molybdenum plate (of inner and outer surface) passed 20 cycles in sintering furnace of uranium dioxide are presented in Fig. 3.

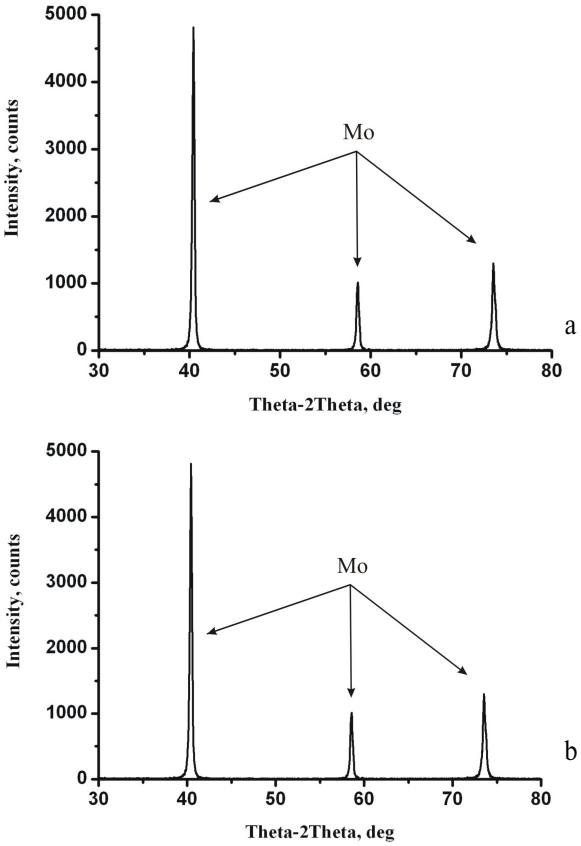

Fig. 3. *The diffraction pattern of molybdenum plate of: a) inner and b) outer surface*

Comparing micrographs of molybdenum plates it is seen that thickness of surface layer in which there is a great amount of defects of structure, channels and carbide and nitride phases extracted on molybdenum grain surface amounts to 0,1 mm for the initial molybdenum plate and for molybdenum the surface of which was protected with niobium film it is 0, 03 mm. Inner surface of molybdenum protected with niobium contains less quantity of structure defects.

Discussion of the results

Molybdenum which is used in nuclear industry at sintering tablets from uranium dioxide represents polycrystalline metal. Presence of the developed system of interior separation surfaces (grain boundaries, subgrains

and secondary phases) mainly determines its physicochemical, mechanical, electrophysical and other properties. Grain-boundary processes controlled by diffusion play an important or even determinative part in developing plastic deformation, structure degradation and metal polycrystal damage. The latter is obviously observed at high temperatures when plastic deformation and especially polycrystal damage is connected with interior separation surfaces first of all with grain boundaries. In such conditions plastic forming is realized by the combined action of various mechanisms: dislocation sliding, diffusive mass transfer, sliding along grain boundaries, and grain motion as a whole [4, 5].

Influence by diffusive flows from the environment (hydrogen which is used as a reducer of uranium oxides; gaseous compounds of nitrogen and hydrogen which were formed at thermal decomposition of aluminium nitrate and polyvinyl alcohol of bounding materials; water vapors which are added in minor amounts to hydrogen atmosphere; oxygen extracted from uranium oxides) changes the state of thin near-surface molybdenum layers which influence greatly in their turn on the development of deformation and destruction processes on microlevel. Change of surface layer structure is seen well at all samples passed 20 sintering cycles of uranium dioxide, Fig. 2.

Impurity atom diffusion at grain boundaries from thin near-surface layers results in significant decrease of durability owing to premature failure at grain boundaries. This phenomenon causing solid-metal fragility is also revealed at a number of polycrystal metals [4].

The carried out investigations allow saying that niobium protecting film prevents formation of carbide and nitride phases at molybdenum grain boundaries; grain surface has less amount of defects.

Conclusion

Niobium coatings on molybdenum at temperatures: in the region of niobium iodide formation – 800 °C and in the region of niobium precipitation – 1200 °C were obtained by gas-transport reaction technique at the laboratory device.

It was stated by electron microscopic analysis that the thickness of molybdenum surface layer with great number of defects amounts to 0,1 mm for pure molybdenum and for molybdenum with protecting niobium coating it is 0,03 mm.

Roentgenophase analysis of molybdenum samples tested in industrial conditions showed that molybdenum composition on outer surface differs considerably from volumetric composition. The presence of Mo_2C and Mo_2N different modifications is typical for outer surface and in the volume of molybdenum sample these phases were not observed.

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