Effect of pulsed electron beam irradiation on the grain boundary heterodiffusion in ultrafine-grained molybdenum

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Abstract. Profiles of depth distribution of nickel concentration in the ultrafine-grained molybdenum after isothermal homogenizing annealing and surface irradiation by a pulsed electron beam in a non-melt regime were determined by Auger spectroscopy methods. It was established that the mutual penetration of molybdenum and nickel atoms is activated in the surface layer as a result of electron beam irradiation, and the diffusion regime in the grain boundaries is changed in comparison with that observed under the homogenizing annealing. Indicated changes are shown to be associated with an increase in the dislocation density in the surface layer and the appearance of additional internal stresses caused by the electron beam exposure.

1. Introduction

Recently, surface modification by electron and ion beam exposure is used to improve the performance characteristics of materials and create protective coatings [1, 2]. Large gradients of temperature and stresses arisen in the surface layers of the material under the electron and ion beam exposure lead to the formation of defects [3, 4]. The rate of radiation-induced defect formation under the electron and ion beam exposure at the temperatures lower than \(0.4T_{\text{melt}}\) is known to be higher than the rate of their annealing [4]. Under these conditions defects accumulate and interact with other defects available in the crystal; new defects are also formed due to this interaction [4-6]. In a polycrystal, grain boundaries serve as sinks for different kinds of defects [7]. The accumulation of defects in grain boundaries can lead to an increase in their diffusion permeability and, as a consequence, the development of such diffusion-controlled processes as change in grain size, redistribution of impurities and the formation of new phases [4, 8, 9]. This, in turn, affects the properties both modified surface and the entire material [4, 10]. Therefore, recently, interest to studies aimed at research of the diffusion features in polycrystalline materials under simultaneous exposure to temperature and irradiation by electron and ion beams has increased.

On the basis of the above reasoning, the purpose of this work is to investigate the development of grain boundary heterodiffusion under the pulsed electron beam exposure in a non-melt regime using the ultrafine-grained (UFG) molybdenum as an example.
2. Experimental Procedure

The experiments were performed using the molybdenum-nickel system (nickel is the diffusing element) as a material for investigation. Molybdenum in the UFG state was used as the base material. The molybdenum-nickel system has unipolar solubility [11]. Nickel is practically insoluble in molybdenum and segregates along the grain boundaries. In addition, molybdenum has a tendency to intergranular fracture. This allows determining the concentration of the alloying element directly at the grain boundaries using the Auger spectroscopy method for a transverse cross section of fractured samples.

The distributions of grain-boundary misorientations in molybdenum and the grain sizes confined by high-angle boundaries were examined by the method of electron backscatter diffraction (EBSD) in a Quanta 200 3D scanning electron microscope at the accelerating voltage 30 kV. The grain-boundary misorientations were determined with respect to the [100]-axis. The angular resolution during determination of the grain-boundary misorientations was 1°, the scanned area measured 20×20 µm², and the scanning step was 0.1 µm.

The surface of molybdenum specimens coated with a nickel film of ~1 µm thickness were irradiated with pulsed electron beams in a SOLO facility [1], having a pulsed electron source, at 923 K for 15 min. The electron beam parameters were as follows: energy density – 5 J/cm², pulse duration – 50 µs, and frequency 3 Hz. The irradiation was performed in an argon atmosphere at the background pressure 0.02 Pa. The area irradiated with pulsed electron beams was 10×5 mm² and the specimen thickness 0.6 mm. The specimen temperature was measured on the rear side opposite to the irradiated surface.

Isothermal homogenizing annealing of the molybdenum-nickel system was performed in a vacuum 6·10⁻³ Pa at 923 K.

The defect density and the presence of elastic stresses in molybdenum were determined by the standard X-ray diffraction methods, including the grazing angle technique, from the diffraction peak broadening at the half width using a Cauchy approximation [12]. The value of elastic stresses was estimated from the crystal lattice microdistortions.

The distribution of the diffusing impurity (nickel) concentration in depth in the molybdenum after homogenizing annealing and irradiation was determined by Auger spectroscopy methods in a SHKHUNA-2 facility. An Auger analyzer with an energy resolution of 0.7% is placed in an ultrahigh (pressure 10⁻⁷ Pa) vacuum chamber of SHKHUNA-2 facility. The beam diameter was ~1 µm. The error in determination of the impurity concentration in the grain boundaries was 20%.

3. Results and Discussion

It was previously established [13] that the average grain size of the grain-subgrain structure elements of the investigated UFG molybdenum was ~0.59 µm. In this case, the average size of grains bounded by high-angle boundaries is almost 1.5 times larger than the average size of the grain-subgrain structure elements and is equal to 1.12 µm. The average scalar density of dislocations in the molybdenum bulk is found to be ~5·10¹³ m⁻², and the average value of crystal lattice microdistortions 1.2·10⁻¹³. Distribution patterns of grain-boundary misorientations in the UFG molybdenum before and after pulsed electron beam irradiation are presented in figure 1. It can be seen that only one maximum is observed in the region of low-angle boundaries with misorientations of θ<4° in the grain boundary misorientation spectrum of the molybdenum in the initial UFG state (figure 1, a). The total fraction of small-angle boundaries (θ<15°) in the distribution of grain-boundary misorientations is as high as ~40%. The distribution of grain boundaries in the spectrum by large-angle misorientations is practically uniform. As a result of irradiation with a pulsed electron beam at the temperature 923 K in a thin (less than 10 µm) surface layer of molybdenum the fraction of grain boundaries with misorientations at θ<4° is up to approximately 33 %. At the same time, the mean values of the grains bounded by high-angle boundaries and their size distribution in the surface layer and in the bulk after irradiation at a temperature of 923 K practically do not change as compared to the initial state. Consequently, an increase in the fraction of grain boundaries with misorientations θ<4° in the surface layer of molybdenum after this irradiation regime can be associated with the formation of new and/or changes in the distribution of existing dislocations. For example, according to the data given in [6], the...
formation of defects of the dislocation loop type is observed in addition to point defects in polycrystalline molybdenum as a result of the ionizing radiation exposure. The change in the dislocation distribution due to the processes of non-conservative motion was observed in aluminum after irradiation with an electron beam [5].

![Figure 1](image1.png)

**Figure 1.** Distribution patterns of grain-boundary misorientations of the UFG molybdenum before (a) and after pulsed electron beam irradiation (b)

X-ray diffraction studies showed that average scalar density of dislocations ($\rho$) in the surface layer of molybdenum after electron beam irradiation increases from $5 \cdot 10^{13}$ m$^{-2}$ to $2.5 \cdot 10^{14}$ m$^{-2}$, and value of crystal lattice microdistortions ($\varepsilon$) – from $1.2 \cdot 10^{-3}$ to $5.8 \cdot 10^{-3}$. In the main bulk of irradiated molybdenum, $\rho$ and $\varepsilon$ values decrease to $10^{13}$ m$^{-2}$ and $8 \cdot 10^{-4}$, respectively, as compared to initial state. This is evidence of tempering of deformed structure of main bulk of the material under the simultaneous temperature and irradiation exposure.

Concentration profiles of the nickel distribution in depth of penetration ($y$) from the surface along the grain boundaries of the UFG molybdenum after homogenizing annealing (curve 1) and after pulsed electron beam exposure (curve 2) at 923 K are represented in figure 2a. It can be seen that the nickel concentration ($J$) at molybdenum grain boundaries after isothermal homogenizing annealing gradually decreases in penetration depth of molybdenum bulk.

A section with a low rate of nickel concentration change in depth corresponding to the molybdenum layer closed the surface is observed on the profile of nickel distribution in depth at grain boundaries of the UFG molybdenum after electron radiation with an electron beam. At the same time, the maximum concentration of nickel at grain boundaries of the molybdenum surface layer after irradiation is three times higher as compared to the annealed state. The concentration profiles of nickel distribution in depth of penetration at grain boundaries of the UFG molybdenum were replotted in the $\ln J - y^2$ coordinates (figure 2b). It can be seen from the figure that indicated profile coincides well with a straight line for the annealed molybdenum. This indicates that nickel diffusion within the grain boundaries of the UFG molybdenum under annealing occurs in the diffusion mode of type C (according to classification [14]). In this case, there is no nickel outflow from the grain boundaries to the molybdenum bulk during the nickel diffusion at grain boundaries. At the same time, for irradiated molybdenum only the final part of the concentration profile of nickel distribution in depth at grain boundaries is described by a straight line in the $\ln J - y^2$ coordinates. Section of the concentration profile of the nickel distribution in depth, corresponding to the area closed to surface, is described in the first approximation by a straight line in the coordinates $\ln J - y^{6/5}$. The direct dependence of $\ln J$ on the value of $y^{6/5}$ indicates that diffusion along the grain boundaries in the region closed to the surface occurs in the diffusion mode of type B (according to classification [14]). Therefore, in part of the molybdenum volume closed the surface the diffusion of nickel along the grain boundaries under irradiation is
accompanied by its outflow into the grain bulk. At the same time, this is not observed during isothermal homogenizing annealing.

Figure 2. Concentration profiles of the nickel distribution in depth of the UFG molybdenum at grain boundaries: a – in the J-y coordinates; b – in the lnJ-y² coordinates (curve 1 – isothermal homogenizing annealing at 923 K; curve 2 – irradiation by pulsed electron beam at 923 K).

Figure 3 shows a typical profile of the nickel distribution in depth in the surface layer bulk of UFG molybdenum after irradiation with a pulsed electron beam.

Figure 3. Concentration profile of the nickel distribution in the bulk of surface layer of the UFG molybdenum after irradiation with a pulsed electron beam at 923 K: a – in the J-y coordinates; b – in the lnJ-y⁶/₅ coordinates.

Two sections (with a high and low gradient of nickel concentration in depth) are observed on the obtained concentration profile after irradiation with an electron beam (figure 3a). Section with a high gradient of nickel concentration in depth corresponds to the region immediately adjacent to the surface, and section with a low gradient is observed in the region remote from the surface. In this case, only a section with a low gradient of nickel concentration in depth is described by a straight line in the coordinates of lnJ-y⁶/₅, i.e. it corresponds to the diffusion mode of type B (figure 3b).

The section of the concentration profile of the nickel distribution in depth in the bulk corresponding to the region immediately adjacent to the surface can be described in a first approximation by the dependence lnJ-y². This dependence corresponds to regime of bulk diffusion of the A type (classification [14]). In the UFG materials, type A diffusion can combine bulk diffusion of the diffusant from the coating directly from the surface and diffusion between the grain boundaries along the grain bulk. The observed deviations of the concentration profiles from those typical for purely diffusion processes apparently can have not only a thermal nature, but are also related to the action of
elastic stress fields formed during irradiation with a pulsed electron beam. It is known [15] that mechanical stresses arising under irradiation exposure promote the acceleration of mass transfer and the formation of complex concentration profiles.

4. Conclusion
Therefore, surface irradiation with a pulsed electron beam in a non-melt regime leads to increase in dislocation density and appearance of additional internal stresses in the surface layer of the UFG molybdenum, and also promotes diffusion processes. At the same time, regime of nickel heterodiffusion at molybdenum grain boundaries can change in comparison with that observed under isothermal homogenizing annealing.

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