CHANGE IN THE STRUCTURAL STATE OF TITANIUM IN ELECTRICAL HEATING IN LIQUID NITROGEN

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Electrical heating in a liquid nitrogen medium alters the structural state of polycrystalline titanium. It is shown by the methods of resistometry, X-ray photography, and metallography that, in treatment by current, grains grow by collective recrystallization, and formation of rutile associated with active diffusion of oxygen is observed.

Investigation of structural materials under extreme conditions in electrothermal action (ETA) in cryogenic media gives information necessary for producing substances with new characteristics. Such investigations are of a very limited character so far [1].

Electrical heating of titanium in liquid nitrogen leads to a substantial change in its structural state, which is embodied in the behavior of the curves of deformation hardening and additional electrical resistance [2]. To elucidate detailed features of the structure modified by electrical heating and instantaneous cooling of titanium in a refrigerant, it is necessary to investigate the role of possible gas saturation of the treated material. In this connection the aim of the present work is the study of the change in the structural state and gas saturation of commercially pure titanium in liquid nitrogen as a result of ETA by the methods of potentiometric measurement of electrical resistance, X-ray photography of polycrystals, and metallography. The VT1-0 commercial titanium studied in the present work is in the initial state in the α-phase; the grain size, according to data of a metallographic investigation, was 6 μm.

Rolled titanium specimens were placed in a tank with liquid nitrogen, and a current with a density of $5 \cdot 10^7$ A/m^2 was passed through them in the pulse regime. The electrical resistance was recorded at 77 K, X-ray photographs and metallographic data on grain sizes were obtained at room temperature before and after ETA. Passage of the current, heating the specimen up to $T \geq 1200$ K, and subsequent cooling of the material down to the refrigerant temperature was taken as one ETA cycle. Qualitative and quantitative analysis of the phase composition of the initial and ETA-treated specimens was performed from Debye powder diagrams (Fig. 1). Photography was performed from the surface of flat specimens in CuK$_\alpha$-anode radiation with an Ni-filter in an RKU-114M chamber. The X-ray photographs obtained were measured photometrically on an IFO-451 microphotometer.

On an X-ray photograph (Fig. 1b) it is seen that after the ETA additional reflexes associated with the emergence of a new phase, namely, the rutile TiO$_2$, appear. Comparing the integral intensity of the initial (α) and new (TiO$_2$) phases enables us to estimate at approximately 25% the amount of rutile in the surface layer of the specimen after the ETA. The thickness of this layer was not determined by a separate investigation; however, from estimating the penetration of X rays into the specimen it can be considered that it is no less than 0.03 mm.

In addition, some diffraction rings divide into separate strong reflexes, which suggests the enlargement of the α-phase grains as a result of collective recrystallization during the ETA. Metallographic analysis showed enlargement of the grain size to 20 μm after the ETA. The angular width of lines from the crystallized grain was much smaller than from the initial one, which suggests removal of stresses.
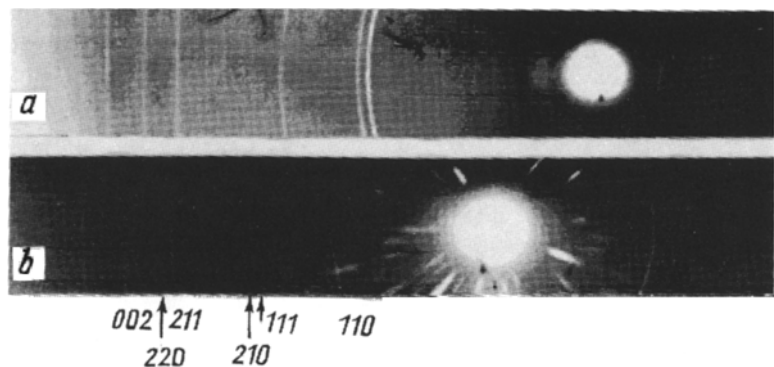

Fig. 1. Debye powder diagrams of the initial polycrystalline titanium (a) and after the ETA (b). Numbers are the indices of the TiO_2 phase planes.
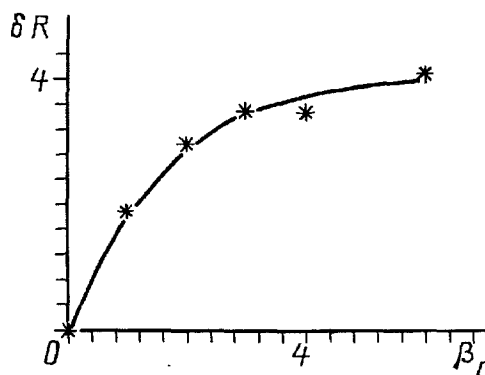

Fig. 2. Relative increase in electrical resistance δR of VT1-0 titanium vs. number of cycles β_c.

High-temperature titanium β-phase is not detected roentgenographically in the specimens after the ETA. The only identified new phase is rutile in spite of the fact that the treatment is performed in liquid nitrogen. At the same time we emphasize that there are two lines of an unidentified phase on the X-ray photographs of the specimens.

The fact that TiO_2 appears in the treated titanium bears witness to active diffusion of oxygen, which is always present in liquid nitrogen, during the ETA. Since in our case there is collective recrystallization during the ETA the behavior of δR (β_c) (Fig. 2) can be considered to be a consequence of two processes: oxygen diffusion and recrystallization. Oxygen, in turn, can affect the electrical resistance of metals through chemical interaction with the matrix and as a result of oxidizing action on dissolved metal impurities. The role of oxygen in the change in the resistance of Ti is substantial due to oxidation of metallic ferro- and paramagnetic impurities in the base metal rather than of the metal itself [3]. In commercially pure titanium the basic impurity of substitution is Fe (0.3%).

Apart from impurities, the change in electrical resistance is affected by mechanical stresses, grain boundaries, defects of the crystal lattice, etc. We will estimate how the temperature difference, which is ΔT > 1200 K in our case, affects the change in electrical resistance during the ETA. The presence of grain boundaries in the material causes the initiation of stresses on them due to anisotropy of the thermal expansion coefficients. This is characteristic of polycrystals, where processes of change in structure under thermocyclic action begin mainly on the grain boundaries and their joints [4].

In the case of Ti the thermal expansion anisotropy $\Delta\alpha$ along the directions of rolling leads to the origination of thermal stresses, which can be estimated from the expression $\sigma_T = E\Delta\alpha\Delta T/(1-\nu)$. At $E = 13.5 \cdot 10^4$ MPa, $\Delta\alpha = 2.3 \cdot 10^{-6}$ K^{-1}, $\Delta T = 1200$ K, and $\nu = 0.3$ the thermal stresses do not exceed 532.3 MPa, which is 1.3 times smaller than the yield point at 77 K [2]. Such stresses originating during the ETA cannot be responsible for the active plastic flow of the treated material or lead to a substantial change in the structural state.

We emphasize that the drastic increase in temperature with the subsequent drastic cooling of titanium during the ETA is accompanined by a martensitic transformation [5]. The allotropic transformation is accompanied by a volume effect, which is apparently caused by the retained orientational and dimensional correspondence. Since the electrical resistance does not depend on the specimen volume, and in our case the monotonic behavior of $\delta R(\beta_c)$ does not undergo a change, the increase in electrical resistance is unaffected by the volume effect during the ETA.

Thus, the martensitic transformation and thermal stresses originating in titanium during the ETA do not play a decisive role in the behavior of $\delta R(\beta_c)$.

The directed movement of interstitial atoms under the action of an electric field [6] is by diffusion as a result of the action of the field forces and the interaction of diffusing ions with electrons. The main contribution is made by diffusion along dislocations and grain boundaries, since the coefficient of diffusion by the defect mechanism is 10^6 times larger than the volume diffusion coefficient [7]. Having high diffusion mobility, oxygen atoms migrate under the effect of the ETA by the above channels of facilitated diffusion, forming new structural states, in particular, rutile inclusions, which radically alter the physicomechanical properties of the treated material.

Taking into account the predominant role of oxygen and its compounds in changing the electrical resistance as well as the established fact that the process of interaction of titanium with gases is determined by diffusion processes in the surface zone [8], we will consider the influence of these processes on the behavior of the dependence of the relative electrical resistance on the number of ETA cycles (Fig. 2). Oxygen, diffusing deep into the metal, forms products of interaction with it only in the surface layer, whose depth depends on the temperature and time of gas saturation, rather than in the entire volume of the specimen. Once the oxide film that divides the metal and the refrigerant has formed on the metal surface, diffusion of the reagent through the film is needed for completion of the reaction. At small ETA times and elevated temperatures a parabolic dependence $\delta R/(\beta_c)$, as Fig. 2 shows, holds, which probably reflects two diffusion processes, acting simultaneously [3]: the movement of anion vacancies with an activation energy of 25.4 ± 1 kcal/mole and the dissolution of oxygen in the metal by interstitial diffusion with an activation energy of 61.8 ± 2 kcal/mole. With this relation of activation energies, the rutile layer apparently forms mainly by the movement of anion vacancies.

On the basis of the relaxation time t_r of vacancies, which depends on their migration energy, the diffusion coefficient (under the assumption of vacancy flow along the grain boundaries) can be estimated from the relation [9] $D_v = 0.1\ d^2/t_r$. The diffusion coefficient calculated for $\beta_c = 6$ is equal to $15\cdot10^{-14}$ m^2/sec, which in the case of movement of anion vacancies, involved in forming the rutile layer, is close in value to the heterodiffusion coefficient of oxygen in titanium at 1223 K: $D = 8.5\cdot10^{-14}$ m^2/sec [10]. The performed comparison of the diffusion coefficients confirms the assumption of a transfer mechanism associated with anion vacancy movement. Thus, the ETA in the medium of liquid nitrogen enables us to control not only the structural state, which changes when large-density currents are passed, but also the diffusion of interstitial atoms over a wide temperature range.

NOTATION

β_c, number of ETA cycles; δR, relative increase in electrical resistance, %; ΔT, temperature change during the ETA; $\Delta\alpha$, change in the thermal expansion coefficient, K^{-1}; E, modulus of elasticity, MPa; σ_T, thermal stress, MPa; ν, Poisson coefficient; d, grain size, m; t_r, time, sec; D, D_v, diffusion coefficient, m^2/sec.

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