CONDENSED-STATE PHYSICS

THE INFLUENCE OF INTERSTITIAL IMPURITIES ON TRUE GRAIN-BOUNDARY SLIDING OF TITANIUM IN COARSE-GRAINED AND SUBMICROCRYSTALLINE STATES

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The structure and temperature dependence of low-frequency internal friction of Grade-2 and Grade-4 titanium specimens following equal-channel angular pressing is investigated. It is established that specimens of both grades in submicrocrystalline states possess a high fraction of high-angle boundaries ($\eta \sim 70\%$) for the average grain size $d \sim 0.8 \ \mu m$. Formation of this structure results in a much lower temperature of initiation and development of true grain-boundary sliding compared to the coarse-grained titanium. It is noted that the grain-boundary sliding activation energy in submicrocrystalline titanium increases with the impurity concentration from 74 ± 4 (Grade-2) to 88 ± 4 (Grade-4) kJ/mol, but is found to be much lower for the coarse-grained recrystallized titanium (140 ± 4 kJ/mol).

Keywords: grain-boundary sliding, internal friction, interstitial impurities, submicrocrystalline structure, Grade-2 and Grade-4 titanium.

INTRODUCTION

One of the mechanisms of deformation of metals and alloys is grain-boundary sliding (GBS) [1–10], associated with mutual displacement of adjacent grains along an interface separating them. There are two types of GBS. True grain-boundary sliding is the GBS which is neither initiated nor accompanied by any plastic deformation inside the grains and is, in terms of physics, an independent primary deformation process. The other type of GBS is an induced GBS initiated and (or) accompanied by intra-grain sliding. Generally, development of GBS is typical for the region of high homological temperatures only ($T > 0.5T_m$). In [9, 11, 12], however, it was experimentally shown that in nanostructured metals GBS also develops at lower temperatures ($T \sim 0.2$–$0.3T_m$), which are close to ambient, or even at room temperature. The authors of [13] put forward an idea of athermal grain-boundary sliding as the principal mechanism of plastic flow of SMC and NC metals and alloys. The lower temperature of manifestation of GBS in submicrocrystalline and nanostructured metals and alloys is due to the fact that with decrease in the grain size the plastic flow mechanism changes from dislocational slip to the mechanisms controlled by diffusion – diffusion-induced creep and grain-boundary sliding. Thus, the above deformation mechanisms in submicrocrystalline and nanostructured metals and alloys compete, and predominance of this mechanism or the other is determined by the grain size.

A very sensitive and selective characteristic of inelastic deformation in solids (including that at the grain boundaries) at low stresses is internal friction [14–17]. According to the numerous experimental studies, the temperature dependence for the internal friction $Q^{-1}(T)$ of recrystallized polycrystalline metals in the general case have two relaxational peaks of internal friction due to the development of inelastic deformation under externally applied

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stress. The low-temperature grain-boundary maximum is associated with high-angle grain boundaries of the ordinary type, while the medium-temperature peak is due to the special and low-angle boundaries. The temperature of the former peak at the vibration frequency $v=1$ Hz is approximately a half of the metal melting temperature, and the activation energy of the process causing this peak is lower than that of bulk diffusion, but higher than the activation energy of grain-boundary self-diffusion.

As any other relaxational peak of internal friction, the low-temperature grain-boundary peak of internal friction is due to inelastic deformation at the boundaries rather than in the bulk. It results from scattering of the elastic vibration energy in the course of inelastic deformation on the grain boundaries under the action of alternating stress. This inelastic deformation might result from grain-boundary sliding and vacancy creep.

The vacancy creep within the temperatures of the low-temperature grain-boundary peak of internal friction is not realized, since its activation energy (it is equal to that of the bulk self-diffusion) is much higher than that of grain-boundary internal friction, which is close to the activation energy of grain-boundary self-diffusion. At the same time, there is similarity between the activation energies of grain-boundary internal friction and true grain-boundary microsliding, which was observed within the temperature range of the low-temperature grain-boundary peak of internal friction. This led the authors of [18–22] to a conclusion that the low-temperature grain-boundary peak of internal friction both in submicrocrystalline and coarse-grained metals is associated with true grain-boundary sliding.

Given the above considerations, we used the method of internal friction to investigate the effect of interstitial impurities on true grain-boundary microsliding in submicrocrystalline titanium.

MATERIAL AND EXPERIMENTAL PROCEDURES

To study the effect of interstitial impurities on true grain-boundary sliding, we used titanium in two grades: Grade-2 with the total content of impurities 0.244 wt.% (0.009 C, 0.006 N, 0.08 Fe, 0.14 O, and 0.009 H) and Grade-4 with the total content of impurities 0.721 wt.% (0.006 C, 0.006 N, 0.35 Fe, 0.34 O, and 0.019 H). Submicrocrystalline structure was formed by severe plastic deformation using the method of equal-channel angular pressing (ECAP) at an angle of 90° between the channels (2 runs through the channels at 723 K, plus 2 runs at 698 K, plus 4 runs at 673 K).

In order to investigate the effect of impurities on true grain-boundary, we measured the temperature dependence of internal friction on the inverse torsion pendulum for the vibration amplitude $\sim 5 \cdot 10^{-6}$. Internal friction was measured within the temperature interval 290–1023 K for the oscillation frequency about 1 Hz during heating at a rate of 400 K/h. From these studies the low-temperature grain-boundary internal-friction peak was obtained.

Titanium structure was examined using a Quanta 600 FEG field-emission scanning electron microscope. Titanium structural state and crystallographic texture were also investigated using the procedure of computer-aided analysis of diffraction patterns from backscattered electrons in a Quanta 600 FEG scanning electron-ion microscope at an accelerating voltage of 20 kV and electron beam currents 13 and 26 nA, using a TexSEM Lab (TSL) software code. Test specimens were prepared using LaboPol-5 (Struers) mechanical grinding-polishing machines; electropolishing of the specimen surfaces was also performed in a LectroPol-5 (Struers) installation in a solution of 60 ml $HClO_4$ + 600 ml CH_3OH + 360 ml $CH_3(CH_2)_2CH_2OCH_2CH_2OH$ at the temperature 278 K and voltage $U = 23$ V.

RESULTS AND DISCUSSION

In the initial state, titanium of both grades exhibited coarse-grained structure with the average grain size 10 μm. Following the severe plastic deformation by ECAP, virtually identical submicrocrystalline states were formed in titanium of both grades, with the size of the elements of grain-subgrain structure about 310 nm, which, as follows from the microstructure pattern (Fig. 1), are predominantly equiaxed particles.

From the data obtained using the method of backscattered electron diffraction, it was found out that as a result of the ECAP treatment a submicrocrystalline structure was formed in titanium of both grades with predominating high-angle GBs, with their fraction being $\eta \approx 70\%$ (Fig. 2a). It is evident from the misorientation distribution bar chart that
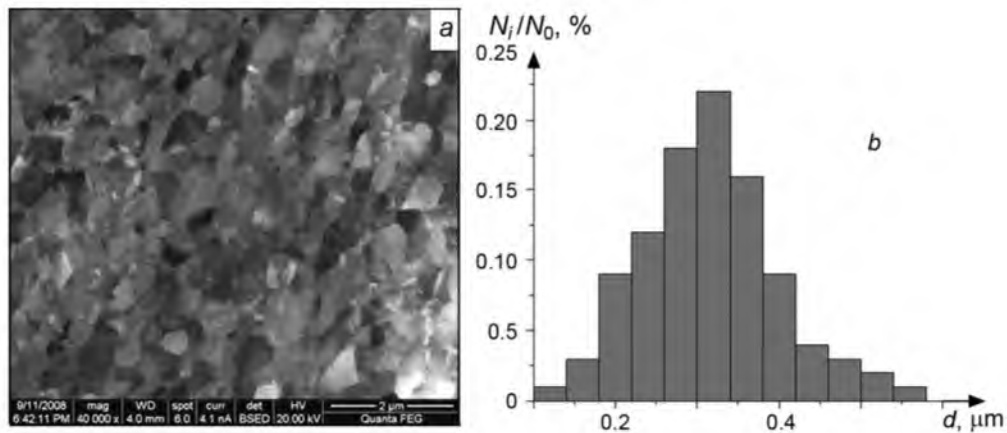
Fig. 1. Microstructure of Grade-4 titanium alloy in the longitudinal section after ECAP (*a*) and the respective structure-element distribution bar chart (*b*).
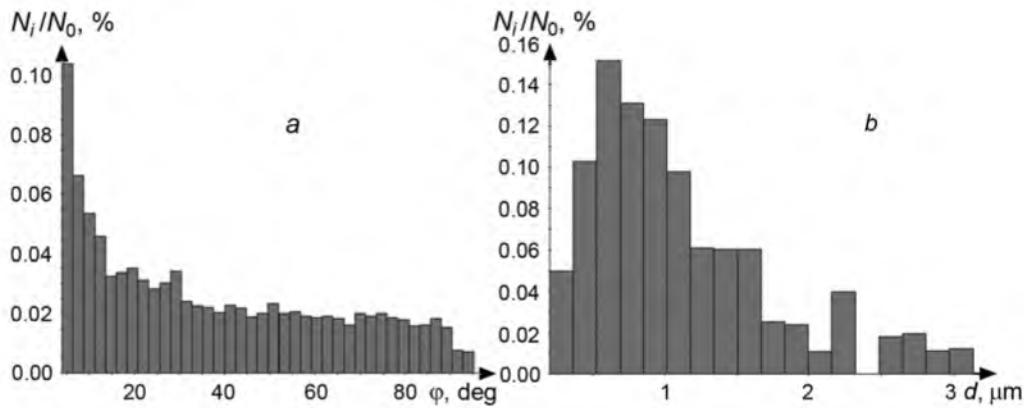

Fig. 2. Distribution bar charts for GB misorientations (*a*) and grain-size distribution for high-angle GBs (*b*) in Grade-4 titanium after ECAP.

there is a large fraction of 3–5° boundaries. An analysis of the GB distribution pattern (Fig. 3*b*) showed that this range of GB misorientation angles is mainly characteristic for abrupted deformation-induced boundries.

It is evident from the distribution bar chart shown in Fig. 2*b* that the size of most grains with high-angle boundaries is as low as 2 μm, with a typical tail formed by quite large single grains. They are elongated along the test-rod axis, and their size in this direction is from 2 to 5–6 μm (indicated by arrows in Fig. 3*b*). The internal structure of these grains is characterized by high density of low-angle boundaries. Note that most part of test specimens did not contain any such grains.

It is well known that the principal role in the development of GBS belongs to high-angle grain boundaries of the ordinary type. Special and low-angle boundaries affect this process to a much smaller degree. As shown above, the Grade-2 and Grade-4 titanium under study after ECAP is characterized by high-angle grain boundaries.

The measurements of internal friction demonstrated that in the initial (coarse-grained) titanium internal friction is intensively increased at the temperatures above 700 K (Fig. 4, curves *1*) and is associated with internal grain-boundary friction. In conformity with the literature data [14, 18–24], the descending (low-temperature) branch of the grain-boundary peak of internal friction is not revealed, since long before the grain-boundary internal friction reaches its maximum value, other relaxational process begin to contribute to internal friction. An examination of the temperature dependence of the relaxed shear modulus testifies that the intense increase in internal friction is due to inelastic
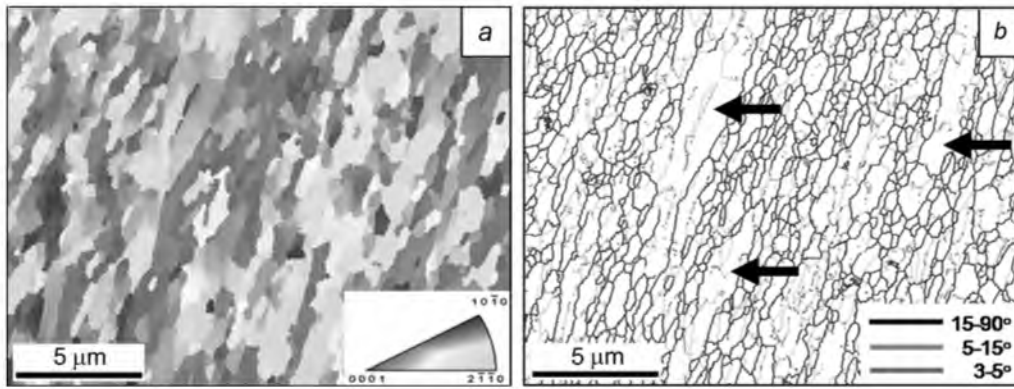
Fig. 3. Distribution patterns of crystallographic orientations (*a*) and grain boundaries with respect to misorientations (*b*) in Grade-4 titanium after ECAP.
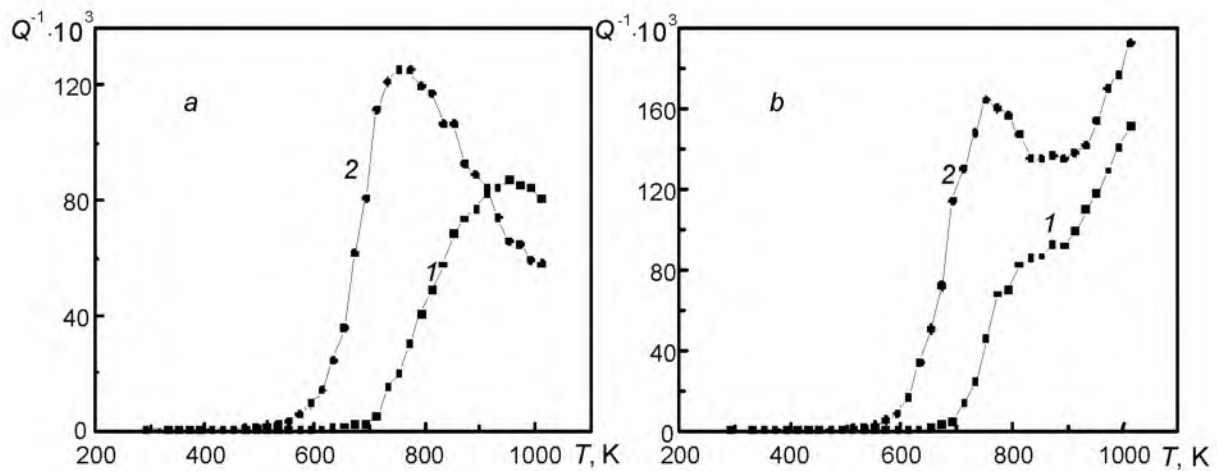

Fig. 4. Temperature dependence of internal friction of Grade-2 (*a*) and Grade-4 (*b*) titanium in coarse-grained (curve *1*) and submicrocrystalline (curve *2*) states.

deformation. In order to determine the relaxed shear modulus we used the data on the temperature dependence for the squared frequency of torsional vibrations of the specimen $(v/v_0)^2$, where v_0 and v are the vibration frequencies at 295 K and at the temperature $T > 295$ K (for torsional vibrations the shear modulus G is proportional to v^2 [17]). It is well known that polycrystals in the temperature range of manifestation of grain-boundary internal friction exhibit a sharp decrease in the relaxational shear modulus, and the dependence $G(T)$ deviates from a linear function [14]. The temperature of the onset of internal friction and abrupt decrease in shear moduli of titanium specimens of both grades coincide (Fig. 4 and 5*a*).

Despite the fact that submicrocrystalline structure was formed at elevated temperatures, in particularly, when relaxational processes might have been taking place, in the course of transition from coarse-grained into submicrocrystalline structure the grain-boundary peak of internal friction shifted to the region of lower temperatures (Fig. 4, curves *2*). It should be noted that in titanium of both grades it was observed at the same temperature $T_m = 760$ K, and that an intensive increase in grain-boundary internal friction also began at the same temperatures. In a way similar to the coarse-grained case, the temperatures of the onset of intensive increase in internal friction and the enhancement of the temperature dependence of the relaxed shear modulus are consistent (Fig. 4 and 5*a*, curves *2*). Thus, the onset of true grain-boundary sliding in Grade-2 and Grade-4 titanium specimens shifted towards the region of lower
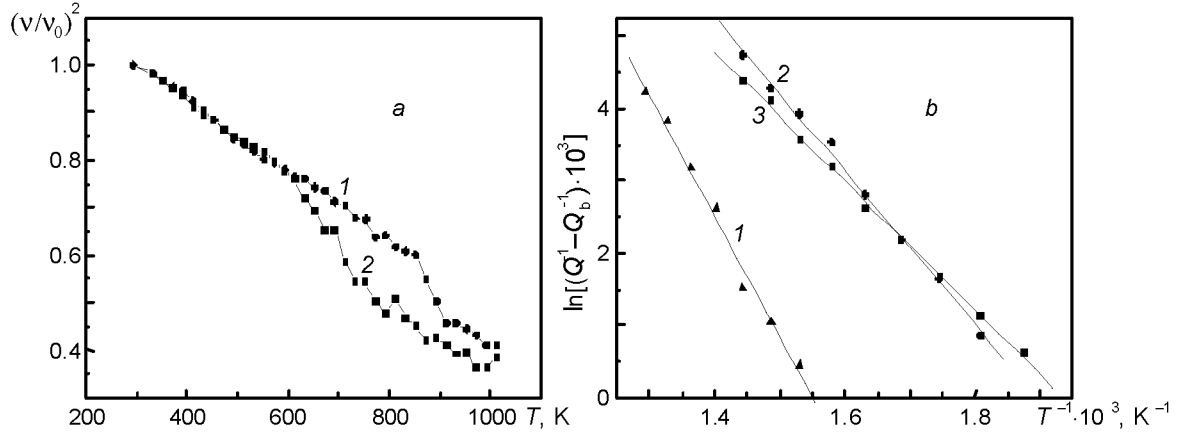
Fig. 5. Temperature dependence of shear modulus of Grade-2 titanium in coarse-grained (curve *1*) and submicrocrystalline state (curve *2*) states (*a*) and the dependence of $\ln[Q^{-1} - Q_b^{-1}]$ on inverse temperature for Grade-4 (curves *1*, *2*) and Grade-2 (curve *3*) titanium in coarse-grained (curve *1*) and submicrocrystalline (curves *2*, *3*) states (*b*).

temperatures as a result of formation of submicrocrystalline structure after ECAP. It is worth noting that neither in the case of coarse-grained recrystallized nor submicrocrystalline states, the temperature of the onset of this process depended on the impurity concentration. The lack of coincidence between the ascending branches of the grain-boundary peaks of internal friction from Grade-2 and Grade-4 titanium specimens testifies to the fact that the activation energy of true grain-boundary sliding depends on impurity concentration.

For the relaxational process with one relaxation time, the internal friction peak is described by the following equation [17]:

$$Q^{-1} - Q_b^{-1} = \left(Q_m^{-1} - Q_b^{-1}\right)\text{sch}\left[\frac{U}{R}\left(\frac{1}{T} - \frac{1}{T_m}\right)\right],\tag{1}$$

and in its ascending branch, as long as $\dfrac{Q^{-1} - Q_b^{-1}}{Q_m^{-1} - Q_b^{-1}} \ll 1$,

$$Q^{-1} - Q_b^{-1} = 2\left(Q_m^{-1} - Q_b^{-1}\right)\exp\left[-\frac{U}{R}\left(\frac{1}{T} - \frac{1}{T_m}\right)\right],\tag{2}$$

i.e.,

$$\ln(Q^{-1} - Q_b^{-1}) = \ln\left[2\left(Q_m^{-1} - Q_b^{-1}\right)\right] - \frac{U}{R}\left(\frac{1}{T} - \frac{1}{T_m}\right).\tag{3}$$

In Eqs. (1)–(3) Q_b^{-1} is the internal friction background, Q_m^{-1} is the value of internal friction at the peak temperature T_m, U is the activation energy, and R is the universal gas constant.

An analysis of the ascending branches of grain-boundary peaks in the temperature dependence of internal friction for the cases of coarse-grained and submicrocrystalline structures demonstrated that the dependence of $\ln\left(Q^{-1} - Q_b^{-1}\right)$ on $1/T$ is linear (Fig. 5*b*), in other words, internal friction occurs due to the same relaxational process

(the value of internal friction at 295 K was assumed to be the background friction Q_b^{-1}). This allowed us to determine the activation energy of internal grain-boundary friction from the tilt of the straight lines $\ln\left(Q^{-1}-Q_b^{-1}\right)$. It turned out that in the course of transition from coarse-grained to submicrocrystalline structure it decreased from 140 ± 4 to 74 ± 4 kJ/mol in Grade-2 titanium and to 88 ± 4 kJ/mol in Grade-4 titanium. For the coarse-grained titanium with perfect grain boundaries, this value of activation energy is consistent with the literature data for other pure metals [14]. It exceeds the activation energy of grain-boundary self-diffusion (97 kJ/mol [25]), but is lower than the activation energy of bulk self-diffusion (151–159 kJ/mol [23, 25]). A similar relation between the activation energy of internal grain-boundary friction and the activation energies of volume and grain-boundary (for imperfect boundaries) self-diffusion is also observed in submicrocrystalline structure.

According to the available experimental data and theoretical estimates [2, 5, 8, 9], the activation energy of grain-boundary diffusion is substantially decreased as the boundary structure becomes less perfect. As shown in [26], the activation energy of grain-boundary diffusion in cobalt in the course of transition from coarse-grained to submicrocrystalline structure decreased from 91 ± 15 to 56 ± 10 kJ/mol. Judging from the literature data [8], in the case of pure metals the activation energies of grain-boundary self-diffusion in coarse-grained and ultrafine-grained titanium should have the same correlation. Hence, it follows that as a result of formation of submicrocrystalline structure in titanium the activation energy of grain-boundary self-diffusion decreases from 97 to $\approx$60 kJ/mol.

The effect of imperfection (degree of nonequilibrium) of the structure of high-angle boundaries of general-type grains on true grain-boundary sliding and its activation energy is due to the diffusion model of this process [8]. According to this model, true grain-boundary sliding is a temperature-activated process and is ensured by the same micromechanism as grain-boundary diffusion. The external stress gives rise to a transition from random motion of voids, formed in the course of delocalization of a vacancy within boundary of a general type, towards their directed motion. It will be accompanied by reciprocal displacement of adjacent grains in the case where the boundary structure is changed, which would result in a decrease in its energy. This rearrangement in the GB structure can take place via diffusion-induced inflow of material from the bulk of the grain or its outflow from the boundary into the bulk of the grain. As a result, for any high-angle boundary of an arbitrary type the activation energy of true grain-boundary sliding would be higher than that of self-diffusion in this boundary, but lower than the activation energy of bulk self-diffusion.

Since the ECAP treatment was performed at elevated temperatures ($T > 670$ K), there is no excessive concentration of vacancies. The activation energy of bulk diffusion would not, therefore, change during transition from coarse- to ultrafine-grained structure. Given this, it follows from the model under study that a decrease in the activation energy of true grain-boundary sliding in the course of formation of ultrafine-grained structure in titanium by the method of equal-channel angular pressing is due to the decrease in activation energy of grain-boundary self-diffusion. This is consistent with the results of investigation of grain-boundary diffusion in coarse- and ultrafine-grained metals [9, 10, 26–30]. First, according to the data in [26–30], in the case of submicrocrystalline structure formed by the methods of severe plastic deformation, the coefficient of grain-boundary diffusion is much higher, while the activation energy is considerably lower than for coarse-grained structure. Second, it is well known [1, 2, 8], that as the grain-boundary energy is increased, the activation energy of grain-boundary self-diffusion is decreased.

SUMMARY

From the results of investigations of microstructure of Grade-2 and Grade-4 titanium it has been established that the submicrocrystalline structure formed by equal-channel angular pressing is characterized by an average grain and sub-grain size of 0.31 µm, with the average grain size in this material being $d \approx 0.8$ µm, and the fraction of high-angle boundaries $\eta \approx 70\%$.

Based on the results of investigation of the temperature dependence of low-frequency internal friction it has been established that Grade-2 and Grade-4 titanium in submicrocrystalline state the true grain-boundary sliding begins and intensively develops at much lower temperatures than it does in coarse-grained structure. It has been shown that activation energy of this process in submicrocrystalline structure increases with increase in the vacancy concentration

from 74 ± 4 (Grade-2) to 88 ± 4 kJ/mol, and is much lower than that for coarse-grained recrystallized titanium (140 ± 4 kJ/mol). It has been proposed that the mechanism controlling true grain-boundary sliding in this case is diffusion.

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