Diffusion-controlled true grain-boundary sliding in nanostructured metals and alloys

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1. Introduction

As a result of submicrocrystalline and nanocrystalline structure formation in metals and alloys under severe plastic deformation not only the grain size, but also the degree of boundary structure perfection changes [1–4]. Grain boundaries in a coarse-grained recrystallized state are perfect: they contain only crystallographically necessary defects whose elastic stress fields are compensated. At the same time, an ultrafine-grained (nano- and submicrocrystalline) structure processed by severe plastic deformation is characterized, along with the small grain size, by imperfect high-angle grain boundaries. They have a much larger free volume and contain both intrinsic and extrinsic grain-boundary dislocations with uncompensated elastic stress fields.

The above structural features of grain boundaries in nano- and submicrocrystalline metals and alloys strongly affect the evolution of the processes occurring at the grain boundaries under thermal and thermal-force action. For example, in materials with non-equilibrium grain boundaries the grain-boundary diffusion coefficient grows by a few orders of magnitude and the temperature of the onset and intensive development of grain-boundary sliding decreases [1–5]. In this connection it is expected that due to a great increase of the grain-boundary fraction in ultrafine-grained materials, the inelastic grain-boundary deformation value should increase, while the growth of the grain-boundary diffusion coefficient should reduce the temperatures of onset and intensive development of true grain-boundary sliding. Thus it is suggested that the peak of grain-boundary internal friction should increase and shift to lower temperatures.

According to well-known models, two types of grain-boundary sliding are known [6,7]. The first one is the true grain-boundary sliding which is not caused and not followed by plastic deformation inside grains and nearby grain-boundary regions. It is the physical primary deformation process which is realized when the acting stress is not high enough to generate dislocations by activating grain-boundary sources and the resistance to dislocation movement in a crystal is low. The second one is induced grain-boundary sliding which is due to and (or) followed by intra-grain dislocation slip. Temperature dependence of internal friction has been used to study these effects [2–4]. The dependence reveals dissipation of energy of oscillations by non-elastic deformation at grain boundaries under applied alternating stress. The true grain-boundary sliding depends on grain size and the detailed state of grain boundaries.

2. Experimental procedures

Regarding the aforesaid, we have comparatively studied how the true grain-boundary sliding manifests itself at different grain structures (coarse-, fine- and ultrafine-grained) using the low-frequency

internal-friction method. For this purpose, an inverse torsion pendulum was used to measure the amplitude-independent internal friction in the temperature range 290–1023 K at oscillation frequency $\nu \approx 1$ Hz. The specimen was heated up with rate 400 K/h. Based on the investigation we determined the grain-boundary internal-friction peak.

The studied materials were commercially pure titanium with various interstitial impurity contents, B2 TiNi-based intermetallics and heterophase Ti–Al–V and Al–Mg–Li alloys. Titanium and the alloys were annealed before testing to form a coarse-grained microstructure with perfect (equilibrium) grain boundaries. An ultrafine-grained microstructure was obtained by severe plastic deformation at elevated temperatures 0.3–$0.5T_m$ (T_m is the melting temperature). The activation energy of true grain-boundary sliding was determined by the ascending branch of the grain-boundary internal-friction peak. In this case, we proceeded from the assumption that the grain-boundary internal-friction results from relaxation occurring at high-angle grain boundaries under alternating loading. Like for any other relaxation process with the same relaxation time, the internal-friction peak is described by the equation [8]:

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

while on the ascending branch, as long as

$$\frac{Q^{-1} - Q_b^{-1}}{Q_m^{-1} - Q_b^{-1}} \ll 1,$$

by

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

i.e.

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

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

3. Results and discussions

3.1. Coarse-grained and submicrocrystalline titanium

The coarse-grained recrystallized titanium with average grain size about 10 m·m and interstitial impurity content from 0.024 to 0.24 mass% demonstrated a qualitatively similar temperature dependence of internal friction (Fig. 1, curve 1). At temperatures T below 700 K the internal friction Q^{-1} varied insignificantly, while in temperature range 700–970 K it sharply increased and then decreased. According to the reference data [9], such dependence of internal friction is typical for the coarse-grained recrystallized titanium with perfect grain boundaries.

Owing to the formation of the submicrocrystalline structure in titanium with average grain size ~300 nm by equal-channel angular pressing (720 K, 8 passed, B_C route, cross angle is 90°) the grain-boundary internal-friction peak is shifted to the lower temperature region, and the maximum value of grain-boundary internal friction increased (Fig. 1, curve 2).

To reduce the grain size and increase structure imperfection of grain boundaries, the submicrocrystalline titanium was subjected to cold deformation by repeated rolling up to high degrees at room temperature (rolling up to 87% results in the average grain size reduction up to 150 nm). These changes in the grain structure exerted no effect on the form of the temperature – internal friction
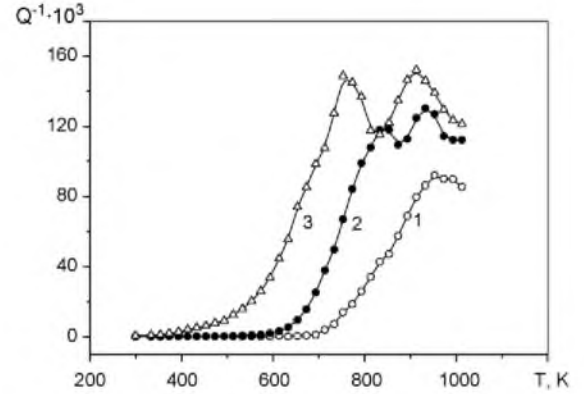

Fig. 1. Temperature dependence of internal friction for titanium with impurity content 0.244% in coarse-grained (1) and ultrafine-grained states with an average grain size of 300 (2) and 150 nm (3).

dependence. They caused, as we expected, further shift of the grain-boundary internal-friction peak to the lower-temperature region and an increase in the maximum value of grain-boundary internal friction (Fig. 1, curve 3).

The asymmetric form of the grain-boundary internal-friction peak and the presence of a second (high-temperature) peak in the $Q^{-1}(T)$ curves for the submicrocrystalline structure allow defining the activation energy only by the ascending (low-temperature) branch of the grain-boundary internal-friction peak. The grain growth starts at the temperature approximately 25 K lower than the temperature of the first maximum.

Analysis of the temperature – internal friction dependence for the coarse-grained and submicrocrystalline titanium on the ascending branch of the grain-boundary peak revealed that the dependence of $\ln(Q^{-1} - Q_b^{-1})$ on $1/T$ is linear (Fig. 2), i.e., internal friction is governed by one relaxation process (the internal friction value at 295 K was taken as the internal friction background Q_b^{-1}). Thus, we determined the activation energy value of grain-boundary internal friction using the slope of the $\ln(Q^{-1} - Q_b^{-1}) - 1/T$ lines. For titanium with 0.244 mass% of interstitial impurities after the submicrocrystalline structure formation it reduced from 144 ± 4 to 85 ± 4 kJ/mol (Fig. 2, curves 1 and 2), while for titanium with 0.024 mass% of interstitial impurities from 140 ± 4 to 73 ± 4 kJ/mol. The decrease of grain-boundary structure perfection at the initial
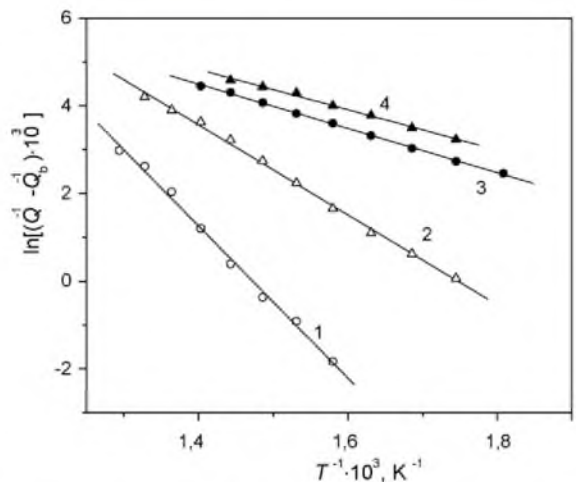

Fig. 2. Dependence of $\ln(Q^{-1} - Q_b^{-1})$ on reciprocal temperature for coarse-grained (1, 3) and ultrafine-grained (2, 4) titanium: (1, 2) as received states; (3, 4) after cold plastic deformation.

coarse-grained and submicrocrystalline structure at ultimate cold plastic strain reduced the activation energy of grain-boundary internal friction. For the initial coarse-grained structure it reduced from 144 ± 4 to 45 ± 4 kJ/mol, and for the initial submicrocrystalline structure from 85 ± 4 to 38 ± 4 kJ/mol (Fig. 2).

For the coarse-grained titanium with perfect grain boundaries the activation energy value corresponds to the reference data for other pure metals [10]. It exceeds the activation energy of grain-boundary self-diffusion (97 kJ/mol [11]), but is lower than the activation energy of bulk self-diffusion (151–159 kJ/mol [9,11]). The same ratio between the activation energy of grain-boundary internal friction and activation energies of bulk and grain-boundary (for imperfect boundaries) self-diffusion is also observed for titanium with submicrocrystalline structure.

According to the known experimental data and theoretical estimates [2,6,12], the activation energy of grain-boundary diffusion decreases noticeably at a growing degree of boundary structure imperfection. As shown in [2], in the studied titanium with 0.244 mass% of interstitial impurities the formation of submicrocrystalline structure at temperature about $0.3T_m$ results in a decrease of the activation energy of cobalt grain-boundary self-diffusion from 91 ± 15 to 56 ± 10 kJ/mol. Judging from the reference data [12], for pure metals the activation energies of grain-boundary self-diffusion in coarse- and ultrafine-grained titanium should approximately be in the same ratio. Thus due to the ultrafine-grained structure formation in titanium the activation energy of grain-boundary self-diffusion decreases from 97 to about 60 kJ/mol.

Hence, the temperatures of onset and intensive development of true grain-boundary sliding (grain-boundary microsliding) in submicrocrystalline titanium decreases due to the activation energy reduction as a result of structure formation with imperfect grain boundaries.

3.2. Coarse-grained and submicrocrystalline alloys

The influence of grain-boundary structure imperfection on true grain-boundary sliding has also been revealed for alloys using the internal-friction method. The investigation of grain-boundary internal friction was conducted for there types of alloys: B2 TiNi-based intermetallics, $\alpha + \beta$ alloys Ti–Al–V and alloys of system Al–Mg–Li.

Prior to the submicrocrystalline structure formation by equal-channel angular pressing (ECAP) the TiNi-based intermetallics were annealed for 1 h at 1073 K with subsequent water quenching. After such thermal treatment the all intermetallics had a coarse-grained structure with perfect grain boundaries. Under severe plastic defor-
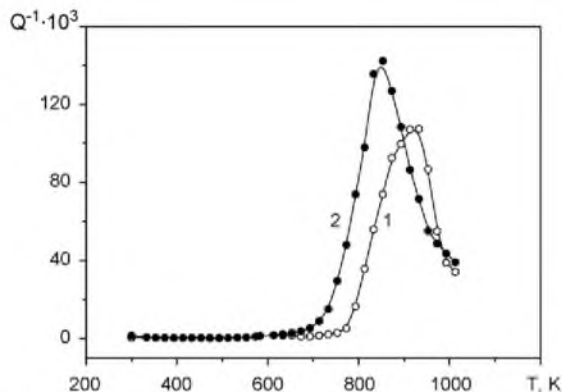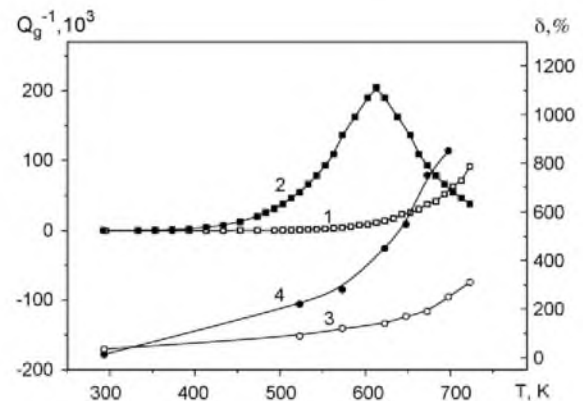
Fig. 4. Temperature dependence of internal friction on GB (1, 2) and elongation up to failure (3, 4) for aluminum 1421 alloy in coarse-grained (1, 3) and ultrafine-grained states.

mation by ECAP at 723 K (8 passed, B_C route, cross angle is $90°$) the intermetallics structure was changed for submicrocrystalline with imperfect grain boundaries (average grain size is about 300 nm). For the both grain structures of all studied intermetallics the temperature dependence of internal friction demonstrates a pronounced grain-boundary internal-friction peak. As in the case of titanium with submicrocrystalline structure it is also shifted to the lower temperature region. As an illustration, Fig. 3 depicts temperature dependences of internal friction for alloy Ti$_{49.4}$Ni$_{50.6}$ (at.%) in the coarse-grained and submicrocrystalline states.

For the heterophase Ti–Al–V and Al–Mg–Li alloys, after the ultrafine-grained structure formation by severe plastic deformation at elevated temperatures ($T \sim 0.5T_m$) the grain-boundary internal-friction peak also shifted to the lower temperature region. In this case, the lower is the temperature of severe plastic deformation, i.e., the higher is the grain-boundary structure imperfection, the more pronounced is the shift of the grain-boundary peak.

Analysis of the temperature – internal friction dependence on the ascending branch of the grain-boundary peak has shown that for the both grain structures of the studied alloys, like for titanium, it is described by Eq. (2), i.e., at the given temperatures internal friction is governed by one relaxation process. Thus, using the slope of the $\ln(Q^{-1} - Q_b^{-1}) - 1/T$ lines we determined the activation energy value of true grain-boundary sliding. In all studied B2 intermetallics as well as Ti–Al–V and Al–Mg–Li alloys the activation energy was found to decrease in transition from the coarse-grained to submicrocrystalline structure. For example, in alloy Ti$_{49.4}$Ni$_{50.6}$ it reduces from 212 ± 5 to 124 ± 5 kJ/mol.

Analysis of the temperature – internal friction dependences, strength and plasticity characteristics has revealed that in submicrocrystalline heterophase alloys Ti–Al–V and Al–Mg–Li the temperatures of onset and intensive development of superplastic flow coincide with those of true grain-boundary sliding (Fig. 4). Such coincidence between the superplastic flow and grain-boundary internal friction was also found earlier for bismuth–tin alloys [13].

4. Conclusions

The study of grain-boundary internal friction has shown that formation of submicrocrystalline structure in metals and alloys by severe plastic deformation at elevated temperatures shifts the onset and intensive development of true grain-boundary sliding (grain-boundary microsliding) to the lower-temperature region and strongly reduces the activation energy of this process. However, the activation energy of true grain-boundary sliding for both the

Fig. 3. Temperature dependence of internal friction for Ti$_{49.4}$Ni$_{50.6}$ alloy in coarse-grained (1) and ultrafine-grained (2) states.

coarse-grained and submicrocrystalline structure exceeds the activation energy of grain-boundary self-diffusion, which corresponds to a given structural state of grain boundaries in the coarse-grained and submicrocrystalline state, but is lower than the activation energy for bulk diffusion. An increase of grain-boundary structure imperfection by plastic deformation at 295 K facilitates true grain-boundary sliding. The activation energy therewith decreases so that it differs insignificantly for the initial coarse-grained and submicrocrystalline structure.

Such effect of the structural imperfection (non-equilibrium degree) of high-angle grain boundaries of a random type on true grain-boundary sliding and its activation energy stems from the diffusion model of this process. According to the model, the true grain-boundary sliding is a thermally activated process and is governed by the same mechanism as grain-boundary diffusion. The applied external stress induces only transition from a random walk of voids, which are formed at vacancy delocalization in the general-type boundary, to their directed motion. The latter is accompanied by the mutual displacement of neighboring grains, which in case of grain-boundary structure rearrangements leads to boundary-energy reduction. The rearrangement can occur through the diffusion inflow of matter from the grain bulk or outflow from the boundary to the grain bulk. As a result, for any high-angle boundary of an arbitrary type, the activation energy of true grain-boundary sliding should be higher than the diffusion activation energy, but lower than the bulk-diffusion activation energy.

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