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Micromechanical properties of grain boundaries and triple junctions in polycrystalline metal exhibiting grain-boundary sliding at 293 K

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Abstract The mechanical properties of grain boundaries (GBs) and the development of grain-boundary sliding (GBS) were studied in the pure Zn using precision microindentation technique, optical, electron and atomic-force microscopy. Results have shown the different dependencies of the microhardness values on the indentation depth for GBs and individual grains. When the size of the plastic zone around the imprint was comparable to the grain size, GBs acted as barriers for dislocation sliding bands and twins. With applying the higher load, more grains were involved in the process of deformation, but microhardness did not increase. That was explained by the activation of GBS, leading to the relaxation processes. In its turn, the microhardness values measured at low loads in the vicinity to GBs and triple junctions (TJs) were higher than those measured in the grain interior. Thus, movement of the ensemble of defects to the GBs during microindentation is the activating factor for GBS in polycrystalline Zn. At the same time, during spreading of the deformation at low loads in the vicinity to GBs the activation of GBS was not observed.

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Introduction

The processes on the grain boundaries (GBs) have an important and often a decisive role in the development of plastic deformation, destruction, strengthening and superplasticity phenomena in polycrystalline materials [1–3]. At low temperatures ($T < 0.2T_m$, where T_m—melting point) GBs act as barriers for dislocation motion. This basic premise of microstructure relations to properties in the materials science has been known as Hall-Petch behaviour. More often the barrier effect leads to the strengthening or brittleness due to the stress concentration at GBs. At $T > 0.2 \div 0.4T_m$ the grain boundary sliding (GBS) processes are possible in many polycrystalline metallic materials. The GBS is a very important mechanism of plastic deformation in the fine-grained metals. GBS processes can either decrease or increase the plasticity of material, depending on the degree of the development of accommodation processes [4–7]. There are many works devoted to the structural investigation of the processes of dislocation interaction with GBs in the conditions of both pile-up at the boundary and GBS [7–9]. However, the scientific interest is caused not only by the structural processes, but also by the mechanical properties of GBs in the conditions of GBS. The studies dedicated to the mechanical properties of GBs are especially relevant in respect to the growing class of nanostructured materials, in which the role of GBs and GBS still remains unclear [10]. In several papers devoted to the GBS studies in the fine-grained materials [10], bicrystals (Zn) [11] and bimetals (Pb/Sn) [12], it has been shown, that the GBS, being a relaxation process, leads to the reduction of stress in the material. For instance, in some superplastic materials (Pb–Sn, etc.) it was observed a softening of GBs which has been caused by the viscous flow along the boundary [12]. It is necessary to note that in the above-mentioned experiments the tension tests have been performed. At the same time to estimate the properties of polycrystalline and single-crystalline materials in the microvolumes the hardness measurements are often used, its role increases along the development of nanohardness testers.

Indentation test is perhaps the most commonly applied method for measuring mechanical properties of polycrystalline materials. This method allows estimating mechanical properties both at grain interior (i.e. in the centre of the grain) and in the region of the GB. Some earlier results concerning GB microhardness of pure metallic materials (Mo, Fe, Nb, Ni, etc.) obtained by different authors have been summed up in [13, 14], where an increase (up to 6–10%) and in some cases even a decrease of GBs microhardness has been demonstrated in comparison to the microhardness of grain interior. However, in these works authors have used comparatively high loads ($P = 0.05$ N), that could lead to the incorrect results due to the higher influence of the properties of grains. The recent nanoindentation experiments [15, 16] using metals with the high melting point (Fe-alloys, Cu and Mo) have revealed a significant hardening effect within a distance of the order of 1 μm from the boundary. In these works the incipient plasticity, dislocation nucleation and transfer across the GB also have been investigated [17]. However, it is necessary to note that the question about microhardness of GBs in the conditions of GBS development in material as well as the question about GBS interrelation to the microhardness of the material has not been studied sufficiently.

The aim of this work was to study microhardness of individual grains, GBs and triple junctions (TJs) in polycrystalline Zn, for which room temperature ($0.42T_m$) is sufficient for the development of GBS process.

The microhardness of GBs areas was investigated using low loads (1.4–14.4 mN). The role of GBS was investigated using the different loads in a wide range 1.4 mN–2 N. It is feasible to spread the plastic zone around the indenter imprint to the boundaries increasing the applied load and to get involved several grains into the process of the deformation. Thus, it is possible to investigate both barrier action of GBs, the occurrence of GBS and to reveal the role of GBS in the microindentation test.

Experimental

The GB processes can be strongly influenced by the impurity segregation, which often induces strengthening effects [18, 19]. In order to avoid the possible segregation effects we have used the highly pure Zn samples. The mechanical properties of GBs were studied using the pure (99.995 at.%) single crystalline and polycrystalline Zn samples. The Zn single crystals were obtained by the directed-crystallization technique [20]. Indentation experiments with single crystal were made on the (0001) surface obtained by the cleavage at low temperature. The polycrystalline samples were prepared by the rolling deformation to the thickness of 1.5 mm at room temperature and further annealing to the average grain size 30–40 μm. After annealing the polycrystalline Zn samples were chemically polished prior to the testing.

Due to the small locality of the measurement the nano- and microindentation allow estimating the mechanical properties directly in the GBs and TJs areas of polycrystalline materials. However, the nanoindentation method has a number of restrictions, from which the most essential one is the requirement for a sample with a very smooth surface. Taking into account the inevitable roughness of sample surface, the microindentation technique has been chosen for this study.

The static microhardness measurements at 293 and 78 K (loading time 15 s) were carried out using the microhardness tester PMT-3M with the modified precision loading device allowing accurate measurements over a wide load range from 1.4 mN to 2 N [21]. The Vickers square pyramid was used in all experiments. The typical accuracy of the measurements of the imprint diagonal (d_{impr}) was 3–7% depending on the load. The indenter penetration depth was calculated as $h = d_{impr}/7$. The creep experiments were made at 293 K with a loading time varying from 2 to 240 s under the load 1 N. The basic results were presented in the form of $H = f(h)$ dependence.

The relative GBs hardening was calculated as $\Delta H_{GB} = (H_{GB} - H_G)/H_G$, where H_{GB} is the GB microhardness and H_G—the average microhardness of the adjacent grains. The relative TJs hardening was calculated in the similar way. The points in the graphics represent the mean values of 5–10 parallel measurements with the 95% confidence intervals of the respective mean values.

For the structural studies around the indentation imprint the optical (Eclipse L150), scanning electron (Evo 50XVR equipped with EDX) and atomic force (CP II) microscopes were used.

Results and discussion

Microhardness measurements of GBs and TJs in Zn

Figure 1 represents the typical indentation imprints made using 1.4 mN load in the centre of the grain, on GBs and on TJs. As it can be seen, the imprints made on GB and TJ have rather symmetrical shape; there are no visible twins or sliding bands around them. In Fig. 2 the microhardness profiles across GBs at three different loads are shown. As it

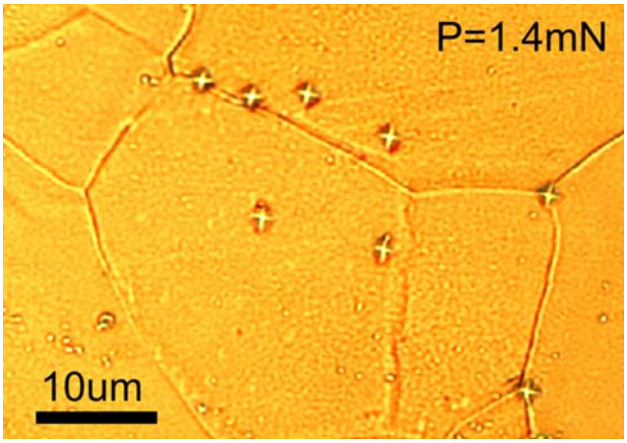

Fig. 1 Micrographs of the indentation imprints made in the polycrystalline Zn at room temperature, $P = 1.4$ mN

is apparent from Fig. 2, the microhardness of GBs is higher than that of the grain. We should note, that the X-ray analysis (EDX) has shown that GBs do not contain excess impurities compared to the volume and the obtained results represent the intrinsic properties of GBs. The zone with the maximal increased values of microhardness (150%) spreads over 1–2 μm away from the GBs. With decreasing of the applied load the GBs hardening effect increased, and at 1.4 mN reached its maximal value (see Table 1). This result could be explained by the relative increase of GB

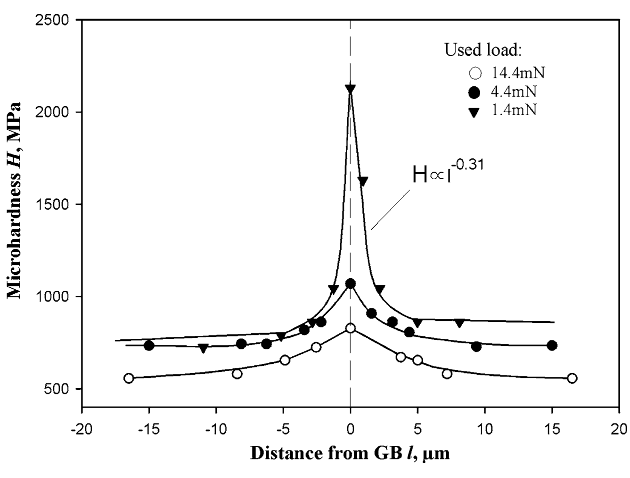

Fig. 2 The microhardness-distance profiles across the grain boundaries in Zn at three different loads (1.4, 4.4 and 14.4 mN) at room temperature

Table 1 The relative GBs and TJs microhardness hardening

P (mN)	ΔH_{GB} (%)	ΔH_{TJ} (%)
1.4	150	105
4.4	50	25
14.4	40	19

properties contribution to the total microhardness. When we put the imprint on the GB the deformation inevitably extends on the areas adjacent to the GB. With the decrease of the load the influence of the GB properties on the deformation process during the microindentation increases. Data from Fig. 2 shows that near to the single boundary, there is a braking of the nucleated dislocations movement. It is possible to assume the observance of Hall-Petch law:

$$H = H_0 + kd^{-0.5},$$

where H, H_0, k and d are the hardness (at a certain load), hardness (at the same load) of grain interior, constant and in our case $d = l$ distance from the GB, respectively. Data fitting to the law $H \propto l^{-m}$ at the load $P = 1.4$ mN has given a value of an exponent $m = 0.31$, which does not fit to the Hall-Petch law with the traditional exponent 0.5 for polycrystalline materials. However, it confirms the barrier function of a single boundary for distribution of a plastic zone at these rather low loads.

The similar result has been obtained for the TJs, which always has the higher microhardness values comparing to the microhardness of adjacent grains. Similarly to the case of GBs, the microhardness of TJs increases, if the applied load decreases. This result is shown in Fig. 3 in the form of the dependence of TJs microhardness on the indentation depth. Here, the exponential law $H = \mathrm{c}h^{-m}$ is observed with a power $m = 0.54$, that probably also confirms the Hall-Petch mechanism. The increase of hardness (ΔH_{TJ}) in the vicinity of TJs is not so high in comparison to the microhardness change in the vicinity of GBs, as it is apparent from the table. This result has shown that during the indentation test more possibilities for stress relaxation are available in the region of the TJ.

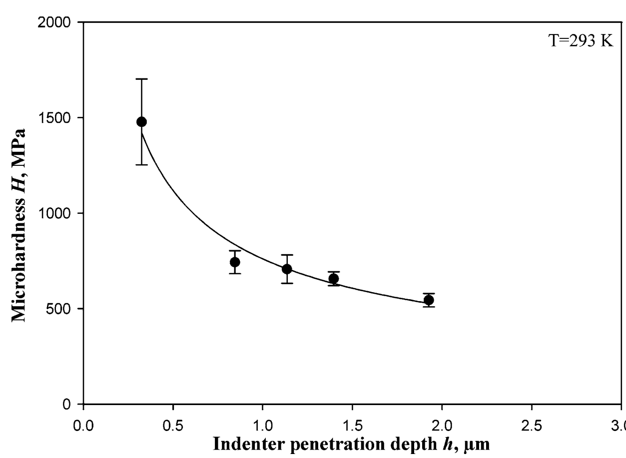

Fig. 3 The microhardness dependence on the indenter penetration depth in the regions of triple junctions in polycrystalline Zn at room temperature

GBS role in microhardness of Zn at 293 K

Experimental data obtained above allowed to assume that the microhardness of the fine-grained Zn would be essentially influenced by the contribution of the properties of GBs, which microhardness is considerably higher than that of grain interior. However, the measurements made at the higher loads ($P > 0.5$ N) have revealed a different result.

As it can be seen from the Fig. 4a, the dependency of microhardness versus indentation depth showed almost identical law for both single crystal and polycrystalline Zn. A more accurate analysis of H (h) curve for polycrystal can reveal three stages (Fig. 4b) during the indentation. When the indentation imprints were put in the centres of the grains at low loads ($P = 1.14$–150 mN), the indentation depth was $h < 2$ μm, $d_{impr} < 14$ μm. Indentation induces the formation of the plastic zone around the imprint with the size $l = f \cdot d_{impr}$, where the coefficient $f > 1$ [22, 23]. We obtain $l < 35$ μm taking $f = 2.5$, which is smaller than the grain size in the sample. In this case the microhardness values are close to those of the single crystalline Zn sample, which is quite obvious. The microhardness decreases when the indentation depth increases (i.e. at low loads) up to a certain constant value. This phenomenon is known as the indentation size effect [21, 24, 25]. Here, for both samples the exponential law $H = \mathrm{ch}^{-m}$ is observed with a power $m = 0.24$, which is in accordance with the data available in the literature for the single crystalline Zn [21]. At higher loads $P = 0.15$–0.2 N (at indentation depth $h = 1.8$–2.5 μm), when the size of the plastic zone is comparable to the grain size, the change of the slope on the curves microhardness versus indentation depth is apparent, that specifies the change in the mechanism of the plastic deformation. In this range of the indentation depths the interaction of the indentation-induced dislocations or twins with the GBs occurs. The structural studies using AFM have shown that at these loads the twins braking at GBs is observed (Fig. 5a). Here, the GBs act as barriers to the motion of dislocations, twins and to the spreading of the

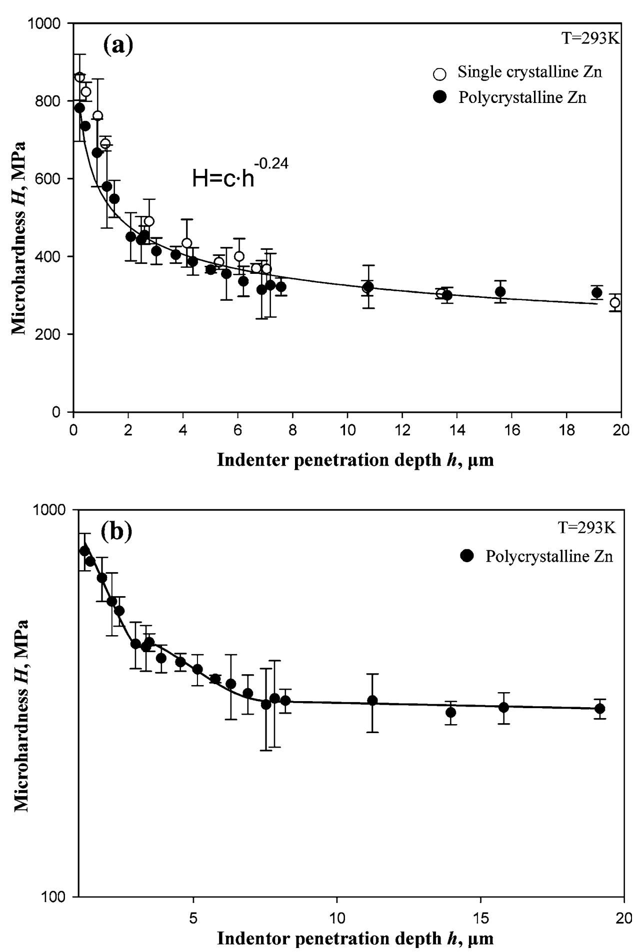

Fig. 4 The microhardness dependence on the indenter penetration depth at room temperature: (**a**) single crystalline and polycrystalline Zn; (**b**) polycrystalline Zn, in semi-logarithmic coordinates

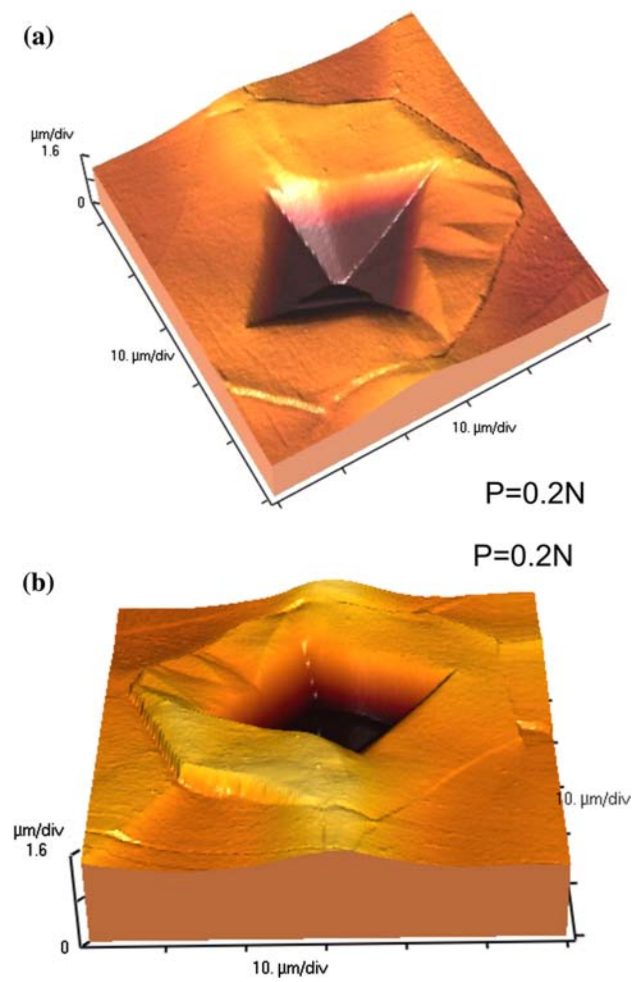

Fig. 5 The AFM image of the plastic zone around the imprint made using $P = 0.2$ N load at room temperature: (**a**) twin braking at the GBs, (**b**) initial stages of the GBS

plastic zone. This result allows estimating the size of plastic deformation zone around the indentation more precisely. If the size of the grain is 40 μm (from Fig. 5a) and the indentation depth is $h = 2$ μm (from Fig. 4b), than the size of the imprint is 14 μm and the size of the plastic zone ($l = 40$ μm) is about 2.8 times bigger than the size of the imprint. In this case, the size of the plastic zone is equal or spreads over the whole grain, the processes of the revealing of GBs, the rise of the separate grains and the grain faceting occur (Fig. 5b).

Using the higher loads ($P > 0.5$ N), when several grains are involved into the deformation process, the microhardness of the polycrystalline Zn is not higher, but sometimes even lower than that of the single crystal. The structural features around the imprint specify the characteristic traces of the GBS processes (Fig. 6a, b) in the adjacent grains: GBs become well outlined and wide, the shape of some sites of grains changes. The GBS is activated due to the pile-up of ensemble of the indentation-induced dislocation and twins at the GBs. The development of GBS determines the lowered microhardness values of the Zn polycrystalline samples in the range of the higher loads.

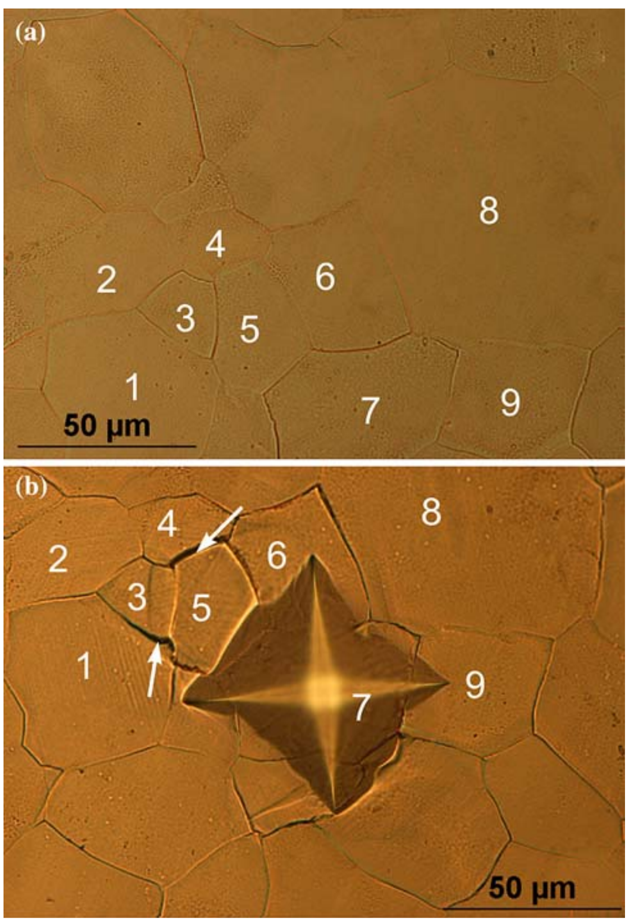

Fig. 6 The micrograph images of the Zn surface before the indentation (**a**) and the same place after the indentation (**b**) using $P = 1$ N. The plastic zone extends over all numbered grains. The changes after indentation in GBs and in the grains are noted by the arrows. The wide, well outlined GBs become apparent after the indentation and the shape of GB sites of grains 1–5 changes. The sliding bands in many adjacent grains (1, 2, 3, 4) become visible after indentation, that testifies to the slip transfer process

The role of temperature and loading time on the occurrence of GBS during indentation tests

As it is known, the GBS is the thermoactivated process and can occur in the polycrystalline materials in temperature-time interval, which is characteristic for GB diffusion ($T > 0.25T_m$). At room temperature the homologous temperature for Zn is $0.42T_m$, so the GBS processes can make a considerable contribution to the plastic deformation of a polycrystalline sample, when the influence of other parameters (time, direction of stress along GB) is excluded. At low temperatures ($T < 0.25T_m$), when the thermoactivated processes are retarded, the GBS does not occur. In order to make sure, that it is the GBS that causes the decrease of the microhardness, the indentation experiments were also performed at 78 K.

As it can be seen from Fig. 7, the microhardness of the polycrystalline Zn is much higher than that of the single crystalline sample. It is particularly notable in the range of $h > 2$ μm, when the plastic deformation extends over many grains. Thus, at low temperature the stresses from the dislocation ensembles in the plastic zone around the imprint do not cause the GBS. GBs act as barriers to the spreading of the plastic zone.

Let as consider the creep process during the indentation at constant temperature and under constant load ($P = 1$ N) but at different loading times (t). The load has been chosen in such way, that under this load the microhardness of the

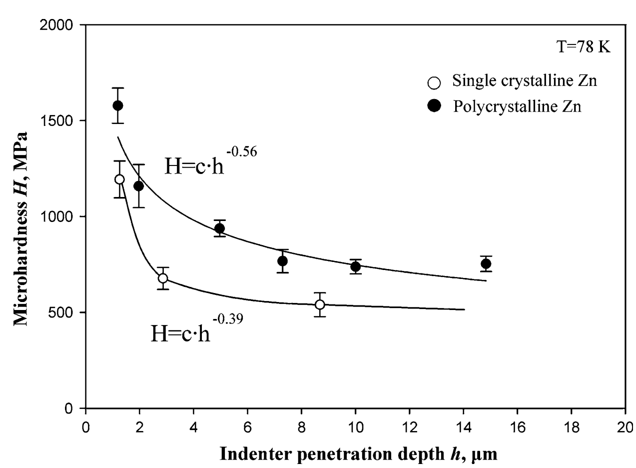

Fig. 7 The microhardness dependence on the indenter penetration depth in the single crystalline and the polycrystalline Zn at 78 K

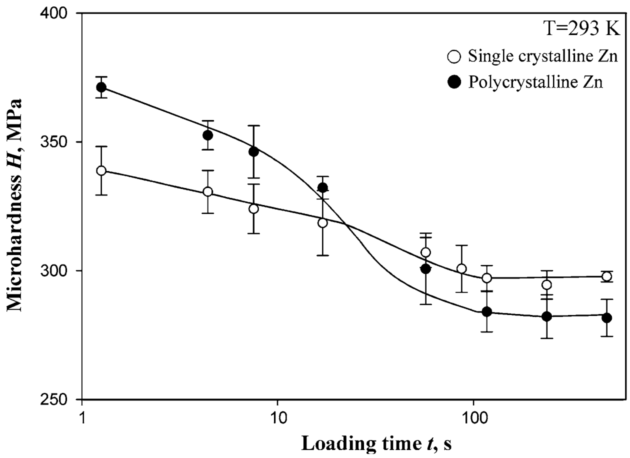

Fig. 8 The creep process in the Zn single and polycrystals under $P = 1$ N load

Zn single crystal and the polycrystalline Zn were identical and the GBS was observed in the standard testing conditions (Figs. 4a, 6). The obtained results are plotted in Fig. 8. When loading time is short ($t = 2$–10 s), the microhardness of the polycrystalline Zn is higher compared to the single crystalline Zn. The hardening effect at $t = 2$ s in the polycrystalline Zn is $\Delta H_{poly}/H = 36\%$ (in relation to microhardness at 240 s), in the single crystalline Zn this effect is not so well pronounced $\Delta H_{mono}/H = 13\%$. Here, it can be deduced that the processes of the GBS development are impeded. In the time interval 30–100 s, the intensive decrease of microhardness of polycrystalline Zn is observed, that is due to the development of the facilitated GBS.

Deformation micromechanisms during the microindentation in the vicinity of GB

The results obtained in this work have shown that the GBS considerably influences the microhardness of the polycrystalline Zn. GBS occurs in the polycrystalline Zn at room temperature during the microindentation test when several grains are involved in the deformation process (i.e. using high loads). The GBS leads to the relaxation of stresses at the GBs and to a decrease in microhardness. At the same time rather high microhardness in GBs areas has been found at low loads. Apparently, the GBS does not occur, or is very insignificant when the indentation is made at low load directly at the GB or in the area of GBs. It is possible to explain these inconsistent results with the features of the microindentation method.

Let us consider the role of the GBs and GBS on the basis of the commonly established dislocation mechanisms of the deformations. A peculiar aspect of the deformation mechanism under the indenter is that, the behaviour of ensemble of interacting dislocation loops (and also twins in Zn), forming the plastic zone, influences the microhardness values, but not the movement of individual dislocations [14].

When the indentation is made in the area of GB, the cooperative movement of nucleated dislocations in the vicinity of the GBs occurs in the non-homogenous medium. Moreover, the acting stresses are mainly normal in the relation to the GB and do not favour the GBS or mass-transfer processes along the boundary despite the relatively high temperature of the experiment (0.42 T_m). Another peculiarity is that the development of the plastic zone around the imprint is constrained by the small volume of the GB area. With decreasing of the indentation load or the distance from GB the role of GB as a barrier increases as it has been shown in the Fig. 2.

The high values of nanohardness in the vicinity of GBs in metals with a high melting point (Cu, Fe–Si, Mo) have also been observed in [15–17]. The authors [16] have not explained this result, but have named it as a “new type” of the size effect. It is difficult to quantitatively compare these results to ours as both studied metals and used testers, loads and indenters were different. However, it is worth noting, that in our experiments the parameter m ($H \propto l^{-m}$), which can be calculated from the GB microhardness profiles (Fig. 2) is higher ($m = 0.31$) than the exponent $m = 0.24$ for the size effect in Zn. Thus, the mechanism of the observed GBs hardening effect at low loads is probably closer to the pile-up mechanism of Hall-Petch.

The situation alters when the imprint is put in the centre of the grain at varying loads (starting with lower to higher). The generation of dislocation loops starts in the medium with the homogenous structure. The moving ensemble of dislocations (or twins) interacts with the GB, which in this case is under influence of shear stress. GB can act as a barrier, that is apparent from Figs. 4b, 5a, but at the higher loads there are various possibilities of the stresses relaxation: dislocation nucleation at grain GBs, transfer of dislocation sliding into the next grain, or even grain boundary movement and GBS [8, 9, 15, 23]. In our case, when the size of the plastic zone is comparable to the grain size, this interaction causes the development of GBS (Fig. 5b). At higher loads the GBS, slip transfer in the adjacent grains and even curvature of the GB line are also visible (Fig. 6b). GBS is relaxation process, it removes barrier action of GBs, provides transfer of the further sliding in grain interior and it determines the fact that the microhardness values of the polycrystalline Zn are identical to those of the single crystal. The GBS in the polycrystalline Zn is activated due to the pile-up of dislocations and twins at the GBs during the microindentation using the high loads. However, the indentation using low loads in the vicinity of GB cannot cause a significant GBS. Thus, it can be deduced that the GBS activation process depends on the load used. Our results have revealed several different mechanisms of plastic deformation during the microindentation test made in the vicinity of GBs, in the individual grain and in the bulk of the polycrystalline Zn.

Conclusions

1. It has been shown, that in the absence of the excess impurities (comparing to the volume) the GBs and TJs have a significant hardening effect in the pure polycrystalline Zn. The zone with the maximal increased values of microhardness spreads over $l = 1–2$ μm away from the GBs. The calculated power $m = 0.31$ in the hardening law $H \propto l^{-m}$ has been observed.
2. The microhardness of the polycrystalline sample measured grain interior, when the plastic zone around the imprint is considerably smaller than the grain size, is equal to the microhardness values of the single crystal. Here, the size effect typical for the Zn single crystal with power $m = 0.24$ has been observed.
3. When the size of the plastic zone is close to the size of the grain the GBs act as barriers to the motion of ensemble of dislocations or twins and to the spreading of the plastic zone. Thus, the process of GBS activation can occur. In this narrow indentation depth range, the microhardness is dependent on the grain size and the ratio imprint diagonal/grain size.
4. When several grains are involved in the process of deformation and under the suitable temperature-time conditions, the microhardness of the polycrystalline Zn decreases. That is connected to the development of GBS. The GBS leads to the relaxation of the stresses at the GBs and facilitates the transfer of the sliding in the adjacent grains.
5. With the decreasing of the experiment temperatures ($T < 0.25T_m$) and indentation time (<15 s), when the thermoactivated processes are retarded, the GBS does not occur, and the microhardness of the polycrystalline Zn increases and is much higher than that of the single crystal. In this case the stresses from the dislocation ensembles in the plastic zone around the imprint do not cause GBS.
6. The motion of the ensemble of defects from the centre of the grain to the GBs is an activating factor for the development of GBS in the polycrystalline Zn during the microindentation at the high loads. At the same time, during the indentation in the area of GB at low loads the activation of the GBS has not been observed.

The obtained results testify to the different mechanisms of plastic deformation during the microindentation test in GBs, in the individual grain and in the bulk of the polycrystalline Zn.

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