

Formation of Nanostructure during High-Pressure Torsion of AI–Zn, AI–Mg and AI–Zn–Mg Alloys

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Abstract. Structure and phase composition of binary Al–Zn, Al–Mg and ternary Al–Zn–Mg alloys were studied before and after high pressure torsion (HPT) with shear strain 300. The size of (Al) grains and crystals of reinforcing second phases decreases drastically after HPT reaching nanometer range. As a result of HPT, the Zn-rich (Al) supersaturated solid solution decomposes completely and reaches the equilibrium state corresponding to room temperature. The decomposition is less pronounced for Al–Mg and Al–Zn–Mg alloys. We conclude that the severe plastic deformation of supersaturated solid solutions can be considered as a balance between deformation-induced disordering and deformation-accelerated diffusion towards the equilibrium state.

Introduction

One of the important ways to improve the mechanical properties of metallic materials is to produce materials with a very small grain size [1]. Among the techniques capable to produce such nanostructured materials those based on severe plastic deformation (SPD) are distinguished. In contrast to the conventional processes of high deformation like rolling or wire drawing, SPD techniques, namely equal channel angular pressing (ECAP) and HPT, do not involve changes in the material geometry, but they lead to a strong grain refinement [2, 3]. One important and still not clarified issue is the role of the diffusion-controlled processes during SPD. Heavy plastic deformation produces many lattice defects, and one can suppose that the vacancy and/or interstitial production during the SPD are high enough to allow diffusion-controlled recovery. It is well known, that vacancies produced during irradiation can induce the diffusion fluxes and permit to reach the thermodynamically equilibrium phase structure at low temperatures [4]. Therefore, one can assume that under some conditions SPD can simultaneously lead to the refinement of the grain structure (the path leading away from the equilibrium) and to release the kinetically suppressed processes of formation of phases which are in the equilibrium at the temperature and pressure of SPD treatment (the path leading away from the equilibrium). In order to clarify this question we have chosen three aluminium based systems, namely Al-Zn, Al-Mg and Al-Zn-Mg which are the base for numerous industrial alloys.

Experimental

Aluminium based alloys of the following composition were under the investigation (the alloys content is indicated in weight percents): Al with 10, 20 and 30% Zn; Al with 5 and 10% Mg; Al with 5%Zn–2%Mg and 10%Zn–4%Mg. The alloys were prepared of high purity components (5N5 Al, 5N Zn and 4N5 Mg) by vacuum induction melting. As-cast disks of these alloys after

grinding, sawing and chemical etching were subjected to HPT at room temperature under the pressure of 5 GPa in a Bridgman anvil type unit (5 torsions, duration of process about 300 s) [5]. All samples for the investigations were cut from the deformed disks at a distance of 5 mm from the sample centre. For this distance the shear strain is ~520 and the equivalent strain value is ~300.

Transmission electron microscopy (TEM) investigations have been carried out in a JEM–4000FX microscope at an accelerating voltage of 400 kV. X-ray diffraction (XRD) data were obtained on a SIEMENS–500 diffractometer (Cu $K_{\alpha l}$ radiation) with a graphite monochromator and line position sensitive gas flow detector.

Results and Discussion

Al–Zn coarse grained (CG) alloys (state before HPT deformation) contain isolated grains of (Zn) solid solution among the grains of (Al) solid solution (Fig. 1a). Both (Al) and (Zn) grains are almost dislocation-free with a dislocation density of about 10^{10} m⁻². The mean grain size in all studied Al–Zn alloys is ~500 µm for (Al) and 3-5 µm for (Zn).



Fig. 1. Microstructure of coarse grained aluminium based alloys: Al-30%Zn (a), Al-10%Mg (b); Al-10%Zn-4%Mg (c).

Al–Mg and Al–Zn–Mg CG alloys also contain grains of two phases (Fig. 1b, c). These are (Al) solid solutions with a mean size of 500 μ m and colonies of intermetallic phases: β -phase (Al₃Mg₂) in Al–Mg alloys (Fig. 1b) and τ -phase (Mg₃₂(ZnAl)₃₉) in Al–Zn–Mg alloys (Fig. 1c) Colony size was about 500 nm. The dislocation density in (Al) is ~10¹² m⁻². XRD data do not reveal



presence of τ and β phases in the alloys, which means that their volume fraction is less than 1%.

Specimens of all studied Al–Zn alloys after HPT have two phases, and two kinds of grains are observed in the structure (Fig. 2). These are (Al) grains with the size of ~800 nm and grains of (Zn) which size is ~200 nm. The dislocation density for these alloys is rather low and is ~ 10^{12} m⁻². It is only slightly higher than in the CG alloys. The grains are practically equiaxial with distinct extinction contours.

Fig. 2. TEM bright field (BF) image of the Al–30%Zn alloy after HPT deformation.

The structures of Al–Mg (Fig. 3) and Al–Zn–Mg (Fig. 4) alloys after HPT are rather similar. Grains with the size of ~150 nm are detected in the structure of both alloying systems. Dislocations are observed to be mainly arranged in subgrain boundaries. Selected area diffraction (SAED) patterns revealed the presence of the β -phase particles in Al–Mg alloy and τ -phase particles. They are uniformly distributed in the material. The particles of the β -phase are extremely dispersed. They are not distinguished in the conventional TEM micrographs and they were detected by the additional spots in the electron diffraction patterns. The grain sizes of the β and τ phases can be estimated to be ~10 nm. X-ray analysis did not detect the secondary phases in these alloys.



Fig. 3. BF (a), dark field (DF) (b) images and SAED TEM pattern (c) of the Al-10%Mg alloy after HPT deformation.



Fig. 4. BF (a), DF (b) images and SAED TEM pattern (c) of the Al-4%Mg-10%Zn alloy after HPT deformation.

For three investigated systems the dependence of the lattice parameter on the alloying element concentration was obtained for both CG and HPT-deformed specimens (Fig. 5). It can be seen from Fig. 5a for Al–Zn alloys that the lattice parameter *a* increases after HPT deformation, therefore, recovering to a value close to that of pure Al. It means that the phase state of the material after HPT deformation is closer to the equilibrium than that for the CG material. In Al–Mg and Al–Zn–Mg alloys the lattice parameter decreases after HPT deformation. However, in these systems such recovery is much less pronounced.



Fig.5. Dependence of the lattice parameter on the alloying element concentration for the Al–Zn (a), Al–Mg and Al–Mg–Zn (b) alloys.

According to the equilibrium phase diagrams, the Al-Zn alloys have to contain the (Al) solid solution with Zn content less than 0.5% and (Zn) solid solution with Al content less than 0.1% at atmospheric pressure and room temperature [6]. In the Al-Mg alloys (Al) solid solution with a Mg content less than 1% and β -phase particles have to be present [6]. The same is true for the Al–Zn– Mg alloys but they contain τ -phase instead of β -phase. Only the volume ratio of these phases is different at different Zn and Mg content. In CG samples the same phases are present, but the (Al) solid solution is in all cases supersaturated at room temperature. HPT deformation at room temperature leads to the decrease of (Al), (Zn), τ and β -phases grain size. It means that HPT produces the less equilibrium grain structure. On the other hand, the supersaturated (Al) solid solution decomposes in all studied samples. It means that HPT results in more equilibrium phase structure. From this point of view, HPT cannot be considered as a cold work, since the phase equilibration proceeds even at room temperature, similar to the warm deformation at moderate strains.

There is a distinct difference between the behaviour of Zn and Mg during the decomposition of supersaturated solid solution under the same HPT conditions. The Al–Zn solid solutions decompose almost completely and reach the equilibrium concentration at room temperature. The decomposition of Al–Mg and Al–Zn–Mg solid solutions proceeds only partly.

The supersaturation is the driving force for the bulk diffusion of Zn and Mg from the solid solution to the sinks which are the particles of (Zn), β and τ phases, respectively. The diffusion paths for individual Zn and Mg atoms would be about 800 and 100 nm, respectively. It corresponds to the bulk diffusion coefficients of $10^{-15} \text{ m}^2 \text{s}^{-1}$ for Zn and $10^{-17} \text{ m}^2 \text{s}^{-1}$ for Mg. The available data for bulk diffusion of Zn in Al give the values of $D (300 \text{ K}) \approx 1.0 \cdot 10^{-23} \text{ m}^2 \text{s}^{-1}$ [7, 8]. Extrapolation of the data for Mg bulk diffusion in Al single crystals gives $D (300 \text{ K}) \approx 1.7 \cdot 10^{-24} \text{ m}^2 \text{s}^{-1}$ [9]. Both values are about 8 orders of magnitude less than those estimated from the diffusion path of the actual solid-solution decomposition during HPT. The question arises: can HPT produce additional

vacancies for acceleration of bulk diffusion, similar to those produced by the irradiation of materials?

Early estimations of the vacancy production during cold work were made based on the data for residual resistivity measurements and gave atomic concentrations of $\sim 10^{-4}$ (which is close to the equilibrium value at the melting point) for strain $\mathcal{E}=1$ [10]. The deformation dependence of the atomic concentration of point defects c may be written as $dc/d\mathcal{E} = \sigma/3\mu$ (μ being the shear modulus, σ being the stress value). Formal application of this relation for our case $\mathcal{E} \approx 400$ results in an enormous value of the total vacancy production during the deformation process (total atomic concentration of 2) which is certainly enough for every equilibration. However, it is unclear, whether the dislocation mechanism for the vacancy production, proposed for low deformations, remains valid for SPD. Therefore, we have to consider the alternative mechanism of GB diffusion.

The transport of Zn from the (Al) matrix can be controlled by grain boundary diffusion of Zn atoms along (Al) GBs. Let us suppose that the moving GBs during HPT swept at least once each Zn atom in the bulk, and then bulk diffusion towards GB has not to be considered. In this case taking into account the possible diffusion path (~1 μ m) and time of the process (300 s) the estimation yields a $D\delta$ value of $1.5 \cdot 10^{-24}$ m³s⁻¹ for a GB thickness of $\delta = 0.5$ nm and a segregation factor s = 1.

In [11] data were obtained for ⁶⁵Zn tracer GB diffusion in the 99.99% pure Al polycrystal within the temperature interval 428–593K. Extrapolation of these data to 300 K yields the value of $sD\delta = 3 \cdot 10^{-24} \text{ m}^3 \text{s}^{-1}$ that is close to the estimation. A similar value of $sD\delta = 10^{-23} \text{ m}^3 \text{s}^{-1}$ is obtained also from [12, 13]. In [14] the parameters of Zn GB diffusion were determined in an Al–30% Zn alloy using the discontinuous precipitation reaction controlled by GB diffusion. The advantage of these measurements is that they were performed at rather low temperatures of 350–500 K. Extrapolation to 300 K yields a $sD\delta$ value of $4 \cdot 10^{-23} \text{ m}^3 \text{s}^{-1}$. Therefore, the GBs in Al provide the diffusion paths for Zn which can be responsible for the decomposition of supersaturated solid solution during HPT.

Data on Mg GB diffusion in Al are not so numerous, eventually due to the lower values of $sD\delta$. The extrapolation of the values obtained in [15, 16] to 300 K yields $sD\delta$ value of $5 \cdot 10^{-28}$ m³s⁻¹. Though the $sD\delta$ values were extracted from the comparison of integral measurements on coarseand nanograined polycrystals obtained by ECAP (as well as in [15]), the data demonstrate undoubtedly a lower GB diffusivity of Mg in comparison with Zn. This fact can explain the slower decomposition of supersaturated solid solutions in Al–Mg alloys studied in the present work in comparison with Al–Zn alloys deformed in the same HPT conditions. Nevertheless, both Zn and Mg GB diffusivities extrapolated towards 300 K are much higher than the $sD\delta$ value for the Al GB self-diffusion (10^{-31} m³s⁻¹ [13]).

If GB diffusion is so effective, why the supersaturated solid solution does not decompose without any HPT? The reason is in the low bulk diffusivity. The solute atoms are frozen in the bulk and cannot reach the GBs. During HPT GBs move sweeping in such a way the "frozen" solute atoms.

High pressure drastically decreases the bulk diffusivity. Minamino et al. measured the Mg diffusivity in Al–Mg alloys at 3.3 GPa by studying the chemical diffusion in polycrystals [17]. Extrapolation of these data to 300 K and 0 % Mg yields D (300 K, 3.3 GPa) = 10^{-27} m²s⁻¹. It is about 3 orders of magnitude lower than at atmospheric pressure (see above). Extrapolation to 5 GPa yields D (300 K, 5 GPa) = 10^{-28} – 10^{-29} m²s⁻¹. The data for Zn GB diffusion under high pressures in Al polycrystals [18] were obtained in conditions similar to [12]. They demonstrate that by extrapolation to 5 GPa the GB diffusivity decreases by 3.5 to 4.7 orders of magnitude depending on the GB class: $sD\delta = 10^{-27}$ m³s⁻¹– 10^{-30} m³s⁻¹. These values are again lower than the estimated $sD\delta$ value of $1.5 \cdot 10^{-24}$ m³s⁻¹ needed for the equilibration of supersaturated solid solution by GB diffusion. It seems that the hypothesis of the additional vacancies produced during SPD (section 4.2) is realistic and can explain the apparent discrepancy.

Conclusions

- 1. Severe plastic deformation by HPT of binary Al–Zn and Al–Mg and ternary Al–Zn–Mg alloys decreases drastically the size of (Al) and (Zn) grains (below 100 nm) and particles of reinforcing phases (below 10 nm). Therefore, HPT with a shear strain of 300 leads to the formation of nanostructures which are further away from the equilibrium state than the initial coarse grained material.
- 2. At the same time, during HPT the Zn-rich supersaturated solid solution (Al) decomposes completely and reaches the equilibruim corresponding to room temperature. This process is less pronounced for the Mg-rich (Al) solid solution. Therefore, HPT results in the formation of a phase structure which is closer to the equilibrium state than that of the initial coarse grained material.
- 3. The most probable mechanism of the equilibration of the (Al) supersaturated solid solution is grain boundary diffusion accelerated by fluxes of vacancies produced due to the SPD and by the sweeping of Mg and Zn atoms from the bulk by moving GBs.
- 4. Therefore, the severe plastic deformation of supersaturated solid solutions can be considered as a balance between deformation-induced disordering and deformation-accelerated diffusion towards the equilibrium state.

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