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Grain boundary films in Al–Zn alloys after high pressure torsion

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In ultra-fine grained Al–Zn alloys after high pressure torsion Al/Al grain boundaries (GBs) completely, partially or pseudopartially wetted by Zn in the solid state have been observed using analytical and high resolution electron microscopy. In the latter case the solid Zn particles in the triple joints form a non-zero contact angle $\theta = 80–160°$ with Al/Al GBs. Simultaneously, a 2–10 nm thick uniform Zn-rich layer is present in the Al/Al GBs.

Keywords: Severe plastic deformation; High pressure torsion; Grain boundaries; Wetting; Phase transformations

During severe plastic deformation (SPD) a steady state is usually reached after a certain strain. The grain size, strength, hardness, hydrogen content, long-range order parameter, composition of phases, etc. stop evolving with increasing strain (i.e. the number of equal-channel angular pressing passes, rotation angle during high-pressure torsion (HPT), or number of accumulative roll bonding passes) [1–3]. Moreover, the structure and composition of phases in the steady state usually differ from those before SPD [4,5]. After SPD phases were frequently found which could also appear after long annealing at a certain temperature T_{eff} [6–13]. One would expect that SPD can force not only bulk but also grain boundary (GB) phase transformations. The phenomenon of GB wetting is known to be very sensitive to the temperature, pressure and composition of phases [14–16]. Usually partial wetting (PW) and complete wetting (CW) of surfaces or interfaces can be distinguished. If a liquid droplet partially wets a solid surface (Fig. 1a) then $\sigma_{sg} - \sigma_{sl} = \sigma_{lg}\cos\theta$, where σ_{sg} is the free energy of the solid/gas interface, σ_{sl} is the free energy of the solid/liquid interface, σ_{lg} is that of the liquid/gas interface and θ is the contact angle. If a liquid droplet partially wets the boundary between two solid grains (Fig. 1b) then $\sigma_{gb} = 2\sigma_{sl}\cos\theta$, where σ_{gb} is the free energy of a GB. Any free surface or GB which is not covered by the liquid droplet remains dry and contains only the adsorbed atoms with a coverage below one monolayer. In the case of complete wetting (Fig. 1c and d) $\sigma_{sg} > \sigma_{lg} + \sigma_{sl}$ or $\sigma_{gb} > 2\,\sigma_{sl}$ the contact angle is zero, and liquid spreads over the free surface or

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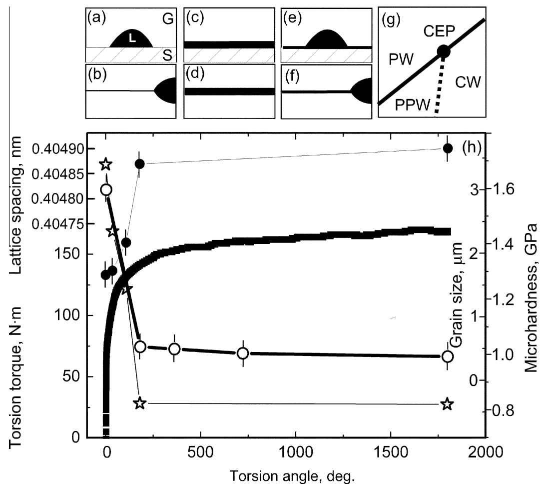

Figure 1. Schemes for the wetting of free surfaces and GBs. (a) Partial surface wetting; (b) partial GB wetting; (c) complete surface wetting; (d) complete GB wetting; (e) pseudopartial surface wetting; (f) pseudopartial GB wetting; (g) generic wetting phase diagram [33]. L, liquid phase; S, solid phase; G, gas phase; PW, partial wetting; CW, complete wetting; PPW, pseudopartial wetting; CEP, critical end point. Thick lines mark the discontinuous (first order) wetting transition, thin lines mark the continuous (second order) wetting transition. (h) Dependence of torsion torque (filled squares), lattice spacing (filled circles [5]), microhardness (open stars [5]) and grain size (open circles) on the HPT rotation angle (strain) for the Al–30 wt.% Zn alloy. The lines are guides for the eye. The values at zero rotation angle were measured after applying a pressure of 5 GPa, but without torsion.

between grains. The PW ↔ CW transition can proceed by the changing temperature and/or pressure [14–17].

The Al–Zn system is a good candidate for the investigation of GB wetting under SPD [2,7,8,18–20]. Various GB wetting transitions proceed in Al–Zn in equilibrium. In (Al) + L and (Zn) + L two phase areas of the Al–Zn phase diagram the transition from partial to complete wetting of (Al)/(Al) GBs and (Zn)/(Zn) GBs by the liquid phase occurs [18]. ((Al) and (Zn) are solid solutions based on Al and Zn.) The wetting phase can also be solid. In the (Zn) + (Al) area the (Zn)/(Zn) GBs can be either partially or completely wetted by a layer of a second solid phase (Al) [19]. Below 205 °C the first (Al)/(Al) GBs completely wetted by solid (Zn) layers appear [20]. HPT of as-cast Al–Zn alloys leads to extremely rapid decomposition of supersaturated Al–Zn solid solutions and almost pure Al and Zn grains appeared instead [2,7]. Al–Zn alloys after HPT have ultra-fine grains and possess extremely high ductility [21,22]. This permits us to suppose that a soft lubricating layer exists along (Al)/(Al) GBs which facilitates GB sliding.

We performed HPT (5 GPa, 300 K, 5 rotations, 1 rpm) of Al-30 wt.% Zn polycrystals made of high purity components. Analytical transmission electron microscopy (TEM) has been performed with a probe-corrected ARM200F JEOL microscope operated at 200 kV. High angle annular dark field (HAADF) images were recorded in scanning mode (STEM) using a probe size of 0.2 nm with a convergence angle of 34 mrad and collection angles in the range 80–300 mrad. To quantify the local Zn concentration energy-dispersive X-ray spectroscopy (EDS) was performed using a JEOL JED2300 detector. Similarly to Mazilkin et al. [2] and Straumal [7], the supersaturated (Al) solid solution almost completely decomposed. The mean Al grain size decreased from 500 μm before deformation to 400 nm after HPT (Fig. 1h).

Figure 1h shows the dependence of torsion torque (filled squares) on the rotation angle (strain) for the Al–30 wt.% Zn alloy. After short work hardening during the first rotation of the anvils the torsion torque reaches a steady state and remains constant. The microhardness (open stars [2]), lattice spacing (filled circles [2]) and grain size (open circles) reach a steady state almost simultaneously with the torsion torque. The micrograph in Figure 2 (right inset) shows a HAADF STEM image where the contrast is related to the local average atomic number (Z-contrast). Thus Zn-rich zones appear bright, while darker areas correspond to Al. The GB between grains 3 and 4 is completely wetted by the solid (Zn) phase and contains a rather thick uniform Zn-rich layer. The plot of the HAADF signal across GB 3/4 (left inset in Fig. 2) has a strong peak with a width of 22 nm. Other (Al)/(Al) GBs in the micrograph are partially wetted. The chain of lenticular (Zn) particles with a non-zero contact angle is visible in the GB between grains 4 and 6. The plots of the HAADF signal across the partially wetted GBs reveal no peaks. In other words, these GBs between (Zn) particles remain completely "dry".

GBs completely and partially wetted by a second solid phase have been observed previously after long annealing in Al–Zn alloys [19,20] and in other systems like Al–Mg [23] or Cu–Co [24]. However, the HPT-treated Al–Zn alloys also contain something unusual, namely (Al)/(Al) GBs with a thin uniform Zn-enriched layer in contact with Zn grains and having a non-zero contact angle. Such a case is shown in Figure 3. The contact area of a Zn grain (left bottom corner) and an (Al)/(Al) GB (aligned from left bottom to right top) is clearly shown (Fig. 3a). The contact angle of the Zn grain

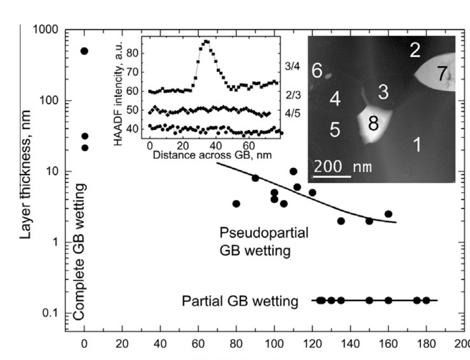

Figure 2. Correlation between the observed thickness of the Zn-rich layer in (Al)/(Al) GBs and the contact angle between Zn particles in the (Al)/(Al) GB triple joints and the respective (Al)/(Al) GBs. Three areas are visible: (1) completely wetted GBs with θ = 0° and a thick GB layer; (2) partially wetted GBs with θ = 120° and 180° without a Zn-rich layer; (3) pseudopartially wetted GBs with θ = 80–160° and thin (2–10 nm) Zn-rich layers. (Right inset) A Z-contrast image obtained by HAADF STEM showing two bright (Zn) grains and six dark (Al) grains. The complete GB wetting layer is visible in the 3/4 GB. A chain of small lenticular (Zn) grains is visible in the 4/6 GB. (Left inset) The HAADF signal intensity across the 2/3, 3/4 and 4/5 (Al)/(Al) GBs.