Defect and Diffusion Forum Vols. 216-217 (2003) pp. 307-312
online at http://www.scientific.net
© 2003 Scitec Publications, Switzerland

Grain Boundary Phase Transitions in the Al–Mg System and Their Influence on High-Strain Rate Superplasticity

B.B. Straumal[1], G.A. López[2], E.J. Mittemeijer[2], W. Gust[2] and A.P. Zhilyaev[3]

[1] Institute of Solid State Physics RAS, Chernogolovka, Moscow District, 142432 Russia

[2] Max Planck Institute for Metals Research and Institute of Physical Metallurgy,
Heisenbergstr. 3, 70569 Stuttgart, Germany

[3] Institute for Physics of Advanced Materials, Ufa State Aviation Technical University, 450000 Ufa,
Russia

Keywords: Grain boundaries; wetting phase transition; high-strain rate superplasticity

Abstract. Grain boundary (GB) wetting phase transitions were studied, for the first time, in Al–Mg polycrystals (Mg contents of 5, 10, 15 and 20 wt.%; temperature range 490–630 °C). It was observed that above 598 °C all GBs in the solid Al-rich phase were wetted by a liquid phase. Below 540 °C no GBs wetted by a liquid phase were observed. The maximal and minimal temperatures of the GB wetting phase transitions, T_{wmax} and T_{wmin}, were determined. Between 540 and 598 °C the percentage of the wetted GBs gradually increases from 0 to 100 %. Grain boundary *prewetting* or *premelting* is given as an explanation for the hitherto not understood high-strain rate superplasticity observed for ternary Al–Mg–X alloys in a narrow temperature range just below the bulk solidus line.

Introduction

It is well known that some of the most important properties of modern materials in high-technology applications are strongly influenced or even controlled by the occurrence of interfaces such as grain boundaries (GBs) and interphase boundaries (IBs) [1]. The study of nanocrystalline solids increased pronouncedly in the last decade. Due to the inherently high concentration of GBs in nanomaterials the understanding of the interface properties has become of great importance. All processes that can change the properties of GBs (and IBs) affect drastically the bulk behaviour of polycrystalline materials. GB phase transitions provide an important example of such processes [2–7]. GB wetting phase transitions have recently been included in the traditional phase diagrams of several systems [7–13].

The occurrence of wetting depends on the GB energy, σ_{GB}. Consider the contact angle Θ between a bicrystal and a liquid phase (Fig. 1). When σ_{GB} is lower than $2\sigma_{SL}$, where σ_{SL} is the energy of the solid/liquid interphase, the GB is non-wetted and $\Theta > 0°$ (Fig. 1a). But if σ_{GB} $2\sigma_{SL}$, the G B is wetted and the contact angle $\Theta = 0°$ (Fig. 1b). The temperature dependence of $2\sigma_{SL}$ is stronger than that of σ_{GB}. If the curves describing the temperature dependencies of σ_{GB} and $2\sigma_{SL}$ intersect, the GB wetting phase transition will occur upon heating at the temperature T_W of their intersection (Fig. 1c). At T T_W the contact angle is $\Theta = 0°$.

The phenomenon of superplasticity has drawn much interest in recent years. Usually superplasticity was observed at relatively low strain rates, typically about 10^{-4} to 10^{-3} s^{-1}. However, it sometimes occurs at extremely high strain rates (up to 10^{2} s^{-1}) [14–19] and in this case it is called high-strain rate superplasticity (HSRS). A small grain size (1 μm) appears to be important for the occurrence of HSRS. Additionally, HSRS has often been observed at temperatures close to the matrix solidus temperature [20, 21].

In the present work, the GB wetting phase transition in the two-phase (S+L) region of the Al–Mg system has been investigated. It will be suggested that the occurrence of *prewetting* or *premelting* is the reason for the observed HSRS.

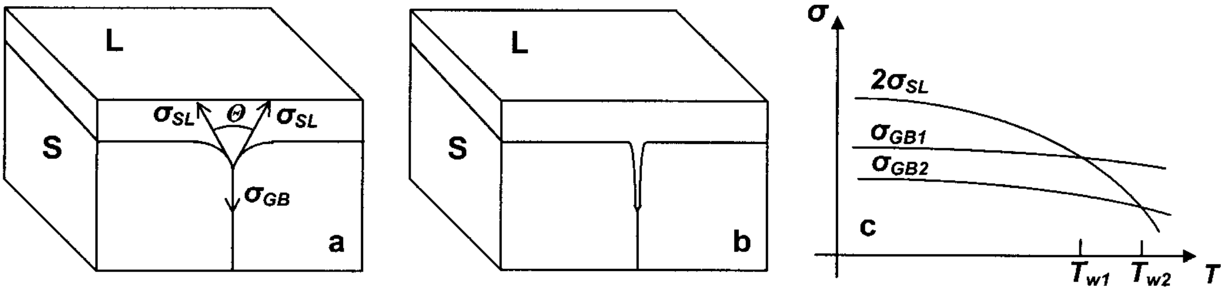

Fig. 1. A non-wetted GB in contact with a liquid phase at $T < T_W$, $\Theta > 0°$ (a). A completely wetted GB, $\Theta = 0°$, T T_W (b). Schematic dependences of $\sigma_{GB}(T)$ and $2\sigma_{SL}(T)$ for two different GBs. They intersect at the T_{W1} and T_{W2} of the GB wetting phase transition (c). L = liquid; S = solid.

Experimental

Al (99.999 wt.%) and Mg (99.95 wt.%) were utilised for the preparation of cylinders (Ø 7 mm) of four Al–Mg alloys with Mg contents of 5, 10, 15 and 20 wt.%. For the wetting experiments, slices (2 mm thick) of the different alloys were cut and sealed into evacuated silica ampoules with a residual pressure of approximately 4×10^{-4} Pa at room temperature. Then, several samples were annealed in furnaces for three days at temperatures between 490 and 630 °C, in steps of 10 °C. The annealing temperature was maintained constant with an accuracy of ±1 °C. After the anneals the specimens were quenched in water. After quenching, for the metallographic analysis the specimens were embedded in resin and then mechanically ground and polished, using 1 μm diamond paste in the last polishing step. The unetched samples were inspected by means of Light microscopy (LM).

A quantitative analysis of the wetting transition was performed adopting the following criterion: every GB was considered to be wetted only when a liquid layer had covered the whole GB; if such a layer appeared to be interrupted, the GB was regarded as a non-wetted GB. Accordingly, the percentage of wetted GBs was determined on the basis of LM analysis. At least 100 GBs were analysed at each temperature.

Results and discussion

Optical micrographs of samples annealed at three different temperatures are shown in Fig. 2. Upon annealing at 610 °C (and at higher temperatures) GB wetting is clearly observed: all GBs were wetted (see the light grey layers at the original GBs in Fig. 2a). Upon annealing at 581 °C just 26 % of the GBs are wetted (Fig. 2b) and no GBs were wetted for annealing temperatures below 540 °C. Partial melting occurred in the interior of grains; however, such a liquid in the interior of the solid phase is isolated (see light grey spots in the interior of the grains). Pores can also be observed in the micrographs (see the black spots). The pores are probably formed during solidification of the liquid by rapid quenching. The fraction of wetted GBs is shown as a function of the temperature in Fig. 3. Between 540 and 610 °C the fraction of the wetted GBs gradually increases with increasing temperature from 0 to 100 %. Therefore, the GB wetting phase transition proceeds in the Al–Mg system between 540 and 610 °C. It means that all GB wetting phase transition tie-lines, one for

°C just 26 % of the GBs are wetted (Fig. 2b) and no GBs were wetted for annealing temperatures below 540 °C. Partial melting occurred in the interior of grains; however, such a liquid in the interior of the solid phase is isolated (see light grey spots in the interior of the grains). Pores can also be observed in the micrographs (see the black spots). The pores are probably formed during solidification of the liquid by rapid quenching. Figure 3 presents the fraction of wetted GBs for every treatment temperature employed in the study. Below 540 °C no completely wetted GBs are present in the sample. Above 610 °C all GBs are completely wetted. Between 540 and 610 °C the fraction of the wetted GBs gradually increases with increasing temperature from 0 to 100 %. Therefore, the GB wetting phase transition proceeds in the Al–Mg system between 540 and 610 °C. It means that all GB wetting phase transition tie-lines for the individual GBs lie between 540 and 610 °C. Consequently, T_{wmin} = 540 °C is the minimal and T_{wmax} = 610 °C is the maximal temperature of the GB wetting phase transition in the Al–Mg system. The respective tie-lines at T_{wmin} and T_{wmax} appear in the two-phase (S+L) area of the Al–Mg bulk phase diagram (Fig. 4). As it was mentioned above, the contact angle Θ depends only on σ_{GB} and σ_{SL}, and not on the relative amount of the liquid and solid phase. Therefore, T_{wmin} and T_{wmax} do not depend on the alloy composition in the two-phase area (S+L).

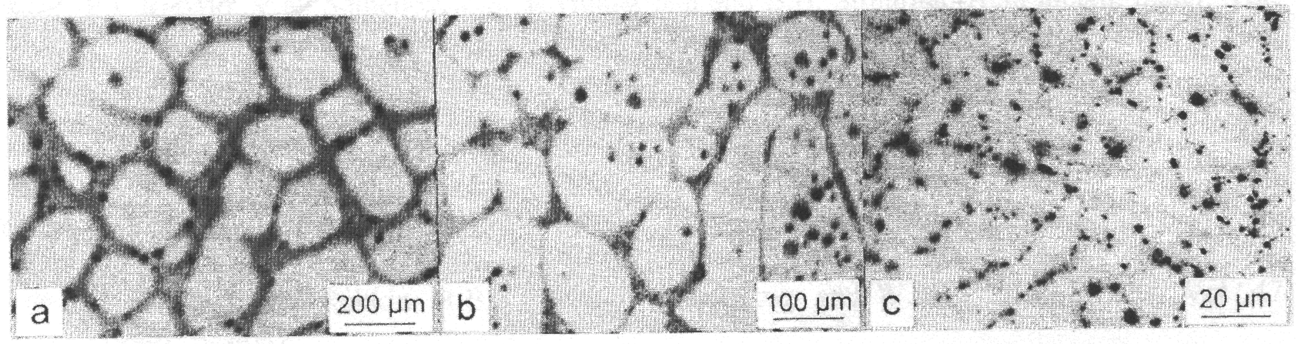

Fig. 2. Optical micrographs of samples annealed at 610 °C (a), 580 °C (b) and 530 °C (c).

Obviously the presence of a liquid phase at GBs affects critically the deformation characteristics of the specimens. Studying pure shear of a commercial Al–5 wt.% Mg alloy Iwasaki et al. [24] found that the shear strain-to-failure drops drastically at the solidus temperature. Above the solidus temperature T_S in the two-phase area (S+L) the shear strain-to-failure is about six times lower than in the pure solid solution.

Previously, it has been shown that GB wetting tie-lines can have the continuation in the one-phase (solid solution) area of the bulk phase diagram, forming in such a way the GB solidus line [2–6, 11, 14, 25]. The GB solidus lines starts at T_S at the intersection of GB wetting tie-line with the bulk solidus and finishes in the melting point T_m. Between the GB solidus and bulk solidus lines a thin layer of the GB (liquid-like) phase exists in the GB. This phase is thermodynamically stable in the GB but unstable in the bulk. The GB covered by a layer of the liquid-like GB phase possesses an enhanced diffusivity [2–5], a strong segregation [6, 11, 26], a high mobility [27] and modified mechanical properties [6, 11, 26]. By the intersection of GB solidus line, the layer of GB phase appears suddenly, and a discontinuity of the first derivative of GB the energy σ_{GB} is observed [26]. Therefore, the tie-line of the first-order GB wetting phase transition in the (S+L) two-phase area can continue in the one-phase solid solution area of the bulk phase diagram as a line of *another* first-order GB (*premeting* or *prewetting*) phase transition. The temperature of this GB phase transition depends on the GB energy and the bulk alloy composition.

In the present work, the tie-lines of the GB wetting phase transition were observed in the two-phase (S+L) area of the Al–Mg phase diagram (Fig. 4). These tie-lines have to continue in the one-micrographs of the Al–Mg–Zn alloys published in [20, 21, 28, 29] do not permit us to estimate $T_{wmin} < T_{w50\%}$. Additionally, most of the triangle of HSRS test lie a short distance underneath the bulk solidus and also the maximal elongation to failure was observed below the bulk solidus [20, 21, 28–31]. This indicates that *prewetting* or *premelting* is indeed responsible for the HSRS in also these alloys.

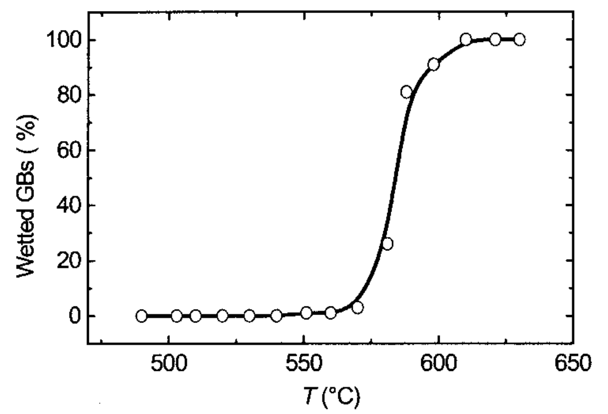

Fig. 3. Temperature dependence of the fraction of wetted GBs in the Al–Mg system.

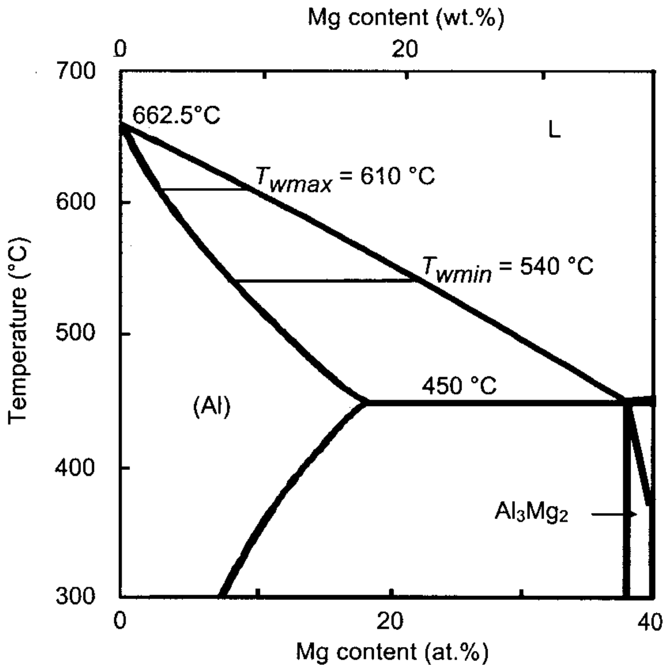

Fig. 4. Al–Mg equilibrium phase diagram [22] and the tie-lines of GB wetting phase transitions (thin lines).

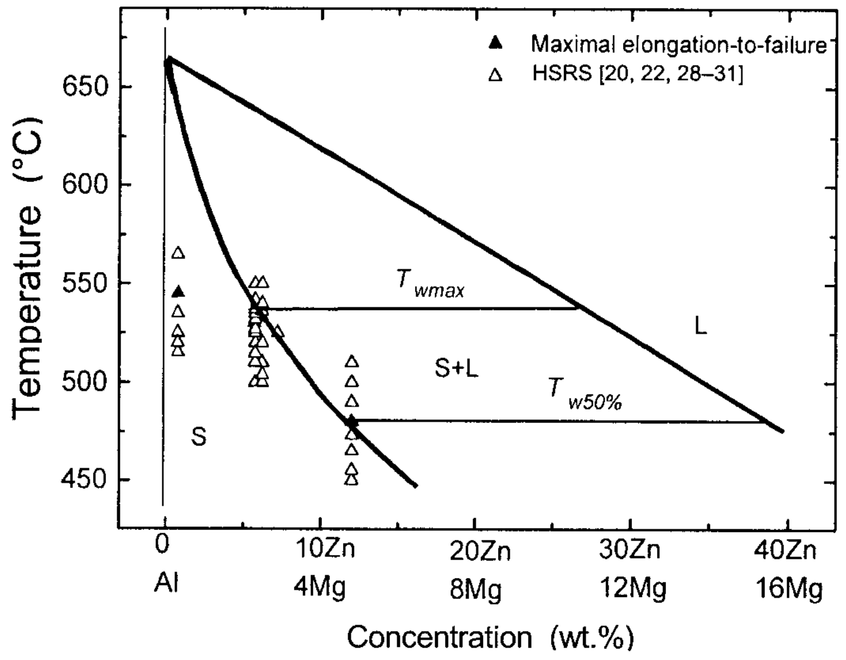

Fig. 5. Pseudobinary phase diagram for 7xxx Al–Mg–Zn alloys (thick lines), containing GB wetting phase transition lines (thin lines).

Conclusions

The Al–Mg system exhibits grain boundary wetting. On the basis of grain boundary wetting data maximal and minimal temperatures, T_{wmax} and T_{wmin}, of grain boundary wetting phase transitions have been indicated and the corresponding tie-lines in the two-phase (S + L) region of the respective bulk phase diagram can be drawn. The occurrence of the grain boundary *prewetting* or *premelting* can be considered as the origin of high strain rate superplasticity upon deformation.

Acknowledgements

The financial support from the Russian Foundation for Basic Research (contract 01-02-16473), the INTAS programme (contract 99-1216) and the German Federal Ministry for Education and Research (contract WTZ RUS 00/209) is acknowledged.

References

[1] T.G. Langdon, T. Watanabe, J. Wadsworth, M.J. Mayo, S.R. Nutt and M.E. Kassner: Mater. Sci. Eng. A Vol. 166 (1993), p. 237
[2] E.I. Rabkin, V.N. Semenov, L.S. Shvindlerman and B.B. Straumal: Acta metall. mater. Vol. 39 (1991), p. 627
[3] O.I. Noskovich, E.I. Rabkin, V.N. Semenov, B.B. Straumal and L.S. Shvindlerman: Acta metall. mater. Vol. 39 (1991), p. 3091
[4] B.B. Straumal, O.I. Noskovich, V.N. Semenov, L.S. Shvindlerman, W. Gust and B. Predel: Acta metall. mater. Vol. 40 (1992), p. 795
[5] B. Straumal, E. Rabkin, W. Lojkowski, W. Gust and L.S. Shvindlerman: Acta mater. Vol. 45 (1997), p. 1931
[6] L.-S. Chang, E. Rabkin, B.B. Straumal, B. Baretzky and W. Gust: Acta mater. Vol. 47 (1999), p. 4041
[7] B.B. Straumal and W. Gust: Mater. Sci. Forum Vol. 207-209 (1996), p. 59
[8] B. Straumal, T. Muschik, W. Gust and B. Predel: Acta metall. mater. Vol. 40 (1992), p. 239
[9] B. Straumal, D. Molodov and W. Gust: J. Phase Equilibria Vol. 15 (1994), p. 386
[10] B. Straumal, V. Semenov, V. Glebovsky and W. Gust: Defect Diff. Forum Vol. 143-147 (1997), p. 1517
[11] L.-S. Chang, E. Rabkin, B.B. Straumal, S. Hofmann, B. Baretzky and W. Gust: Defect Diff. Forum Vol. 156 (1998), p. 135
[12] B. Straumal, W. Gust and T. Watanabe: Mater. Sci. Forum Vol. 294-296 (1999), p. 411
[13] A.P. Sutton and R.W. Balluffi: *Interfaces in Crystalline Materials* (Oxford University Press, New York, 1995), p. 400.
[14] K. Higashi, S. Tanimura and T. Ito: MRS Proc. Vol. 196 (1990), p. 385
[15] M. Mabuchi and T. Imai: J. Mater. Sci. Lett. Vol. 9 (1990) 763
[16] T.G. Nieh, C.A. Henshall and J. Wadsworth: Scripta metall. Vol. 18 (1984), p. 1405
[17] M. Mabuchi, K. Higashi, Y. Okada, S. Tanimura, T. Imai and K. Kubo: Scripta metall. Vol. 25 (1991), p. 2003
[18] T.G. Nieh, P.S. Gilman and J. Wadsworth: Scripta metall. Vol. 19 (1985), p. 1375
[19] K. Higashi, Y. Okada, T, Mukai and S. Tanimura: Scripta metall. Vol. 25 (1991), p. 2053
[20] K. Higashi, T.G. Nieh, M. Mabuchi and J. Wadsworth: Scripta metall. mater. Vol. 32 (1995), p. 1079
[21] Y. Takayama, T. Tozawa and H. Kato: Acta mater. 47 (1999), p. 1263

[22] T.B. Massalski et al. (eds.): *Binary Alloy Phase Diagrams* (ASM International, Materials Park, OH 1993).

[23] H. Iwasaki, T. Mori, M. Mabuchi and K. Higashi: Acta mater. Vol. 46 (1998), p. 6351

[24] J.W. Cahn: J. Chem. Phys. Vol. 66 (1977), p. 3667

[25] J.W Cahn: J. Phys. Colloq. Vol. 43-C6 (1982), p. 199

[26] J. Schölhammer, B. Baretzky, W. Gust, E. Mittemeijer and B. Straumal: Interf. Sci. Vol. 9 (2001), p. 43

[27] D.A. Molodov, U. Czubayko, G. Gottstein, L.S. Shvindlerman, B.B. Straumal and W. Gust: Phil. Mag. Lett. Vol. 72 (1995), p. 361

[28] B. Baudelet, M.C. Dang and F. Bordeux: Scripta metall. mater. Vol. 26 (1992), p. 573

[29] T. Imal, M. Mabuchi, Y. Tozawa, Y. Murase and J. Kusul: *Metal & Ceramic Matrix Composites: Processing, Modelling & Mechanical Behaviour* (TSM-ASME, Warrendale, PA, 1990).

[30] M. Mabuchi, K. Higashi, T. Imal and K. Kubo: Scripta metall. Vol. 25 (1991), p. 1675

[31] N. Furushiro, S. Hori and Y. Miyake, in S. Hori et al. (eds.): *Proc. Int. Conf. Superplast. Adv. Mater. (ICSAM-91)* (Japan Soc. Res. Superplast. Sendai, 1991), p. 557.