GRAIN BOUNDARY WETTING PHASE TRANSFORMATIONS IN THE Zn–Sn AND Zn–In SYSTEMS

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Abstract — The wetting phase transition of grain boundaries (GBs) by the melt has been studied in the Zn – 6 wt.% Sn and Zn – 5.3 wt.% In polycrystals and Zn bicrystals (two [10$\bar{1}$0] tilt GBs with misorientation angles ϕ = 19° and 66°, and one [11$\bar{2}$0] tilt GB with misorientation angle ϕ = 79°, wetting by the In-rich melt). In the Zn – 6 wt.% Sn polycrystals, the fraction of the completely wetted GBs gradually increases from 20 to 70% with increasing temperature between 260 and 400 °C. In the Zn – 5.3 wt.% In polycrystals, the fraction of the completely wetted GBs gradually increases from 20 to 65 % with increasing temperature between 215 and 395°C. Temperature dependences of the contact angle $\theta(T)$ for bicrystals were measured using scanning electron microscopy and light microscopy. θ decreases with increasing T and reaches zero (complete wetting) at a certain temperature T_w. It has been observed for the first time that temperature dependences of contact angle intersect (at about 350 °C). The wetting transformation for Zn GBs is discontinuous (first order): $\theta(T)$ dependence is convex, $d\theta/dT$ has a break at T_w and $\theta \sim ((T - T_w)/T_w)^{1/2}$. Tilt GBs in Zn–Sn and Zn–In systems become completely wetted when about 60-70% of GBs with higher energy are already completely wetted in a polycrystal.

1. INTRODUCTION

The idea that the transition from incomplete to complete surface wetting is a phase transformation was first proposed by J.W. Cahn and Ebner and Saam [1,2]. They first assumed that the (reversible) transition from incomplete to complete wetting can proceed with increasing temperature, and it is a true surface phase transformation. Cahn proposed that in the three-phase area of the phase diagram close to the critical point T_c where two phases become undistinguishable, the wetting transition should occur. This is due to the fact that if α' and α'' phases become undistinguishable at T_c and the β-phase remains unchanged, the energy of the α'/α'' interphase boundary $\sigma_{\alpha'\alpha''}$ tends to zero at the temperature $T \to T_c$. The energy $\sigma_{\alpha'\alpha''}$ would always reduce to lower than the energy of the α'/β (or α''/β) boundary $\sigma_{\alpha\beta}$ above a specified temperature T_w which is close enough to T_c.

Later this idea was successfully applied for grain boundaries (GBs) and old data on GB wetting were reconsidered from this point of view [3–6]. The occurrence of wetting depends on the GB energy, σ_{GB}. Consider the contact angle θ between a bicrystal and a liquid phase. When σ_{GB} is lower than $2\sigma_{SL}$,

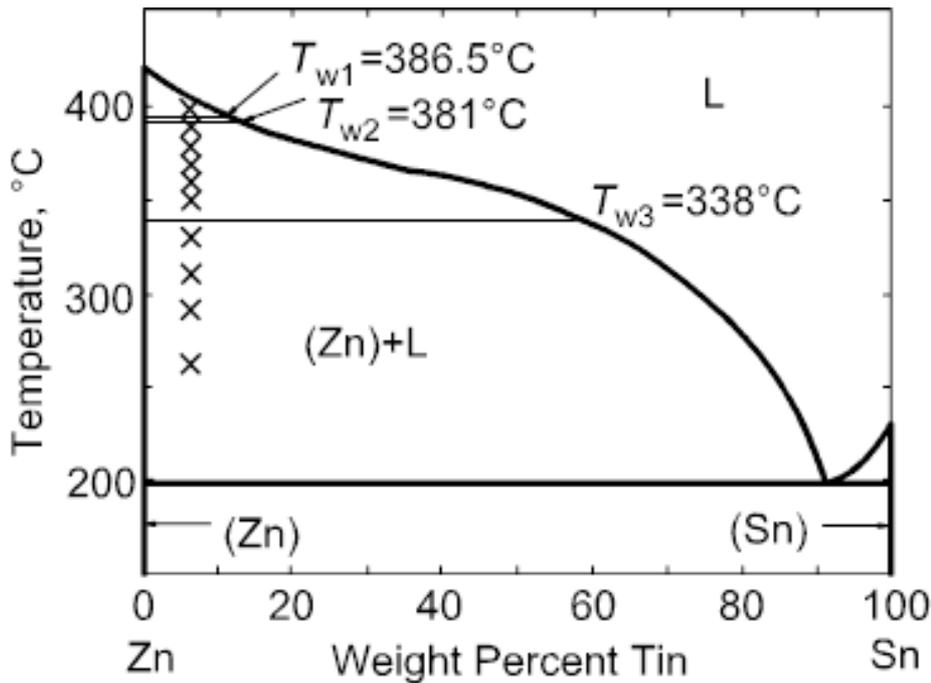Corresponding author: B.B. Straumal, e-mail: straumal@issp.ac.ru
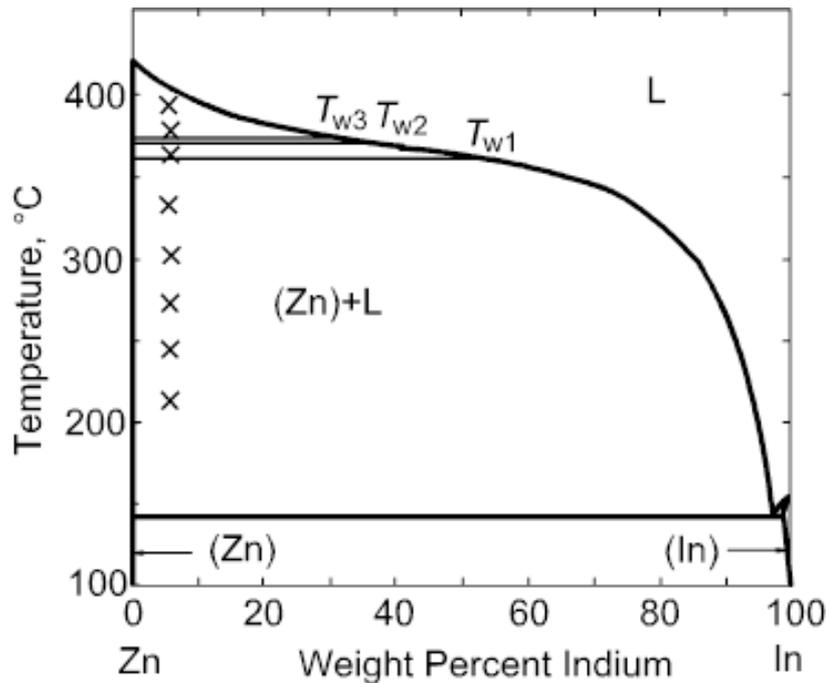
Fig. 1. Zn–In phase diagram. Thick solid lines denote bulk phase equilibria [16]. (Zn) is the single-phase region where only the Zn-based solid solution is in equilibrium in the bulk. L is the single-phase region of a liquid phase (melt). In the (Zn)+L two-phase region the Zn-based solid solution coexists with the melt. Crosses denote the experimental points for the Zn – 5.3 wt.% In polycrystals. Three horizontal thin solid lines in the (Zn)+L region at $T_{w1} = 362$ °C, $T_{w2} = 376$ °C and $T_{w3} = 375$ °C are the tie-lines of the GB wetting phase transformation experimentally obtained in this work for the [10$\bar{1}$0] tilt GBs with misorientation angles $\phi = 19$° and 66° and the [11$\bar{2}$0] tilt GB with misorientation angle $\phi = 79$°, respectively.

where σ_{SL} is the energy of the solid/liquid interphase, the GB is incompletely wetted and $\Theta > 0$°. But if $\sigma_{GB} \geq 2\sigma_{SL}$, the GB is completely wetted and the contact angle $\theta = 0$°. $2\sigma_{SL}$ decreases with temperature increase stronger than σ_{GB}. If the curves describing the temperature dependences of $\sigma_{GB}(T)$ and $2\sigma_{SL}(T)$ intersect below melting (or liquidus) temperature, the GB wetting phase transition will occur upon heating at the temperature Tw of their intersection. At $T \geq Tw$ the contact angle is $\Theta = 0$°. Above T_{wGB} GB is substituted by a layer of the melt. GB wetting phase transformations are important for liquid phase sintering of metals and ceramics [7,8], semi-solid metal processing [9], thixotropic casting [10], exploitation of heat-exchanger tubes filled with liquid metal [11], etc. GB wetting phase transitions have recently been included in the traditional bulk phase diagrams of several systems [3–6,12–15]. Zn–Sn and Zn–In alloys can be the base of the lead-free solders. Therefore, they were chosen for the investigation of GB wetting transitions in this work.

2. EXPERIMENTAL

Zn (99.995 wt.%), Sn (99.995 wt.%) and In (99.999 wt.%) were utilized for the preparation of cylinders (Ø ~ 10 mm) of Zn – 6 wt.% Sn and Zn – 5.3 wt.% In alloys. The alloys were melted in the induction furnace in vacuum of approximately 10^{-5} Pa. For the wetting experiments, slices (2 mm thick) of both alloys were cut and sealed into evacuated duran glass ampoules with a residual pressure of approximately 4·10^{-4} Pa. Then, the Zn – 5.3 wt.% In samples were annealed for 1 h at temperatures between 215 and 395 °C (see Fig. 1). the Zn – 6 wt.% Sn samples were annealed for 1 h at temperatures between 260 and 400 °C (see Fig. 2). The annealing temperature was maintained constant with an accuracy of ±1 °C. After anneals, the specimens were quenched in water, sectioned, embedded into metallographic resin, ground and polished.

Flat Zn bicrystals having the thickness of 2 mm, width of 10 mm and length of 50-100 mm with indi-

Fig. 2. Zn–Sn phase diagram. Thick solid lines denote bulk phase equilibria [16]. (Zn) is the single-phase region where only the Zn-based solid solution is in equilibrium in the bulk. L is the single-phase region of a liquid phase (melt). In the (Zn)+L two-phase region the Zn-based solid solution coexists with the melt. Crosses denote the experimental points for the Zn – 6 wt.% Sn polycrystals. Two horizontal thin solid lines in the (Zn)+L region at T_{w1} = 386.5 °C and T_{w2} = 381 °C are the tie-lines of the GB wetting phase transformation experimentally obtained in [15] for two individual [10$\bar{1}$0] tilt GBs with misorientation angles ϕ = 16° and 60°, respectively. At T_{w3} = 338 °C complete GB wetting was observed in [19,20].

vidual tilt GBs were grown from the Zn of 99.999 at.% purity using the modified Bridgman technique [17,18]. Two [10$\bar{1}$0] tilt GBs with misorientation angles ϕ = 19° and 66°, and one [11$\bar{2}$0] tilt GB with misorientation angle ϕ = 79° in Zn were grown. Since tilt GBs with different ϕ possess different energy σ_{GB}, we also expected different T_w values for them. The bicrystals were cut into pieces of 10 mm length. The layer of the (Zn)+(In) alloy and (Zn)+(Sn) of nearly eutectic compositions was applied on two opposite surfaces of each 2×10×10 mm Zn bicrystal. Individual 2×10×10 mm Zn bicrystals coated by a (Zn)+(In) or (Zn)+(Sn) layers were sealed in the duran glass ampoules, evacuated to 10^{-4} Pa and filled with high purity argon. The coated Zn bicrystals were annealed between 200 and 380 °C during 0.5 h. After annealing the samples were quenched in cold water, sectioned perpendicular to the GB and coated surfaces, embedded into metallographic resin, ground and polished, using 1 µm diamond paste in the last polishing step.

The microstructure was investigated with the aid of scanning electron microscopy (SEM) and light microscopy (LM). SEM investigations were carried out in a Tescan Vega TS5130 MM microscope equipped by the LINK energy-dispersive spectrometer produced by Oxford Instruments. Using the same equipment, the composition of various structural elements in the annealed and quenched samples was controlled with the aid of electron probe microanalysis. Light microscopy was performed using a Neophot-32 light microscope equipped with a 10 Mpix Canon Digital Rebel XT camera. A quantitative analysis of the wetting transition in the polycrystalline samples 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 analyzed at each temperature.
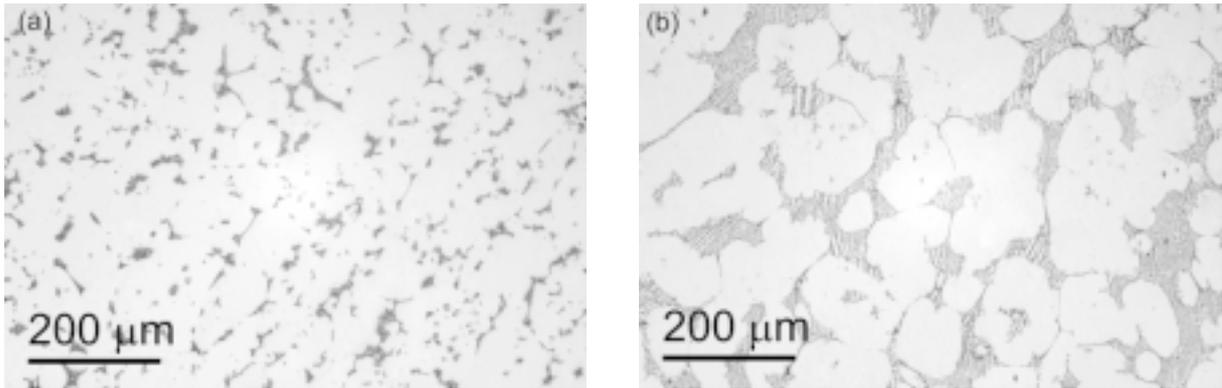
Fig. 3. Microstructure of the Zn – 6 wt.% Sn alloy after annealing at 290 °C, 1 h (a) and at 390 °C, 1 h (b) obtained by light microscopy. Zn-rich matrix appears white; GB wetting layers appear grey.
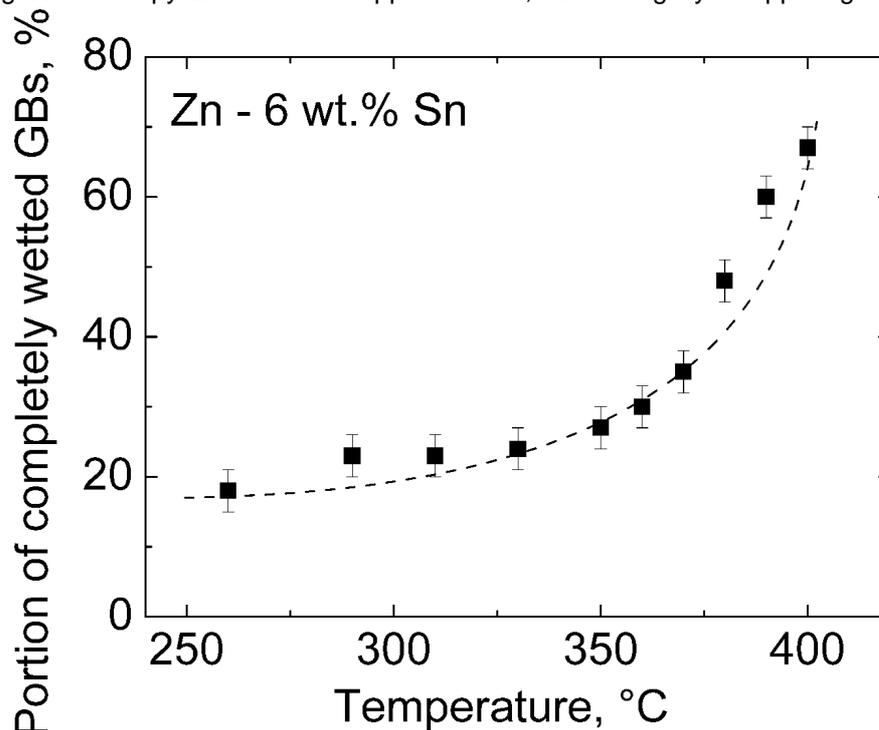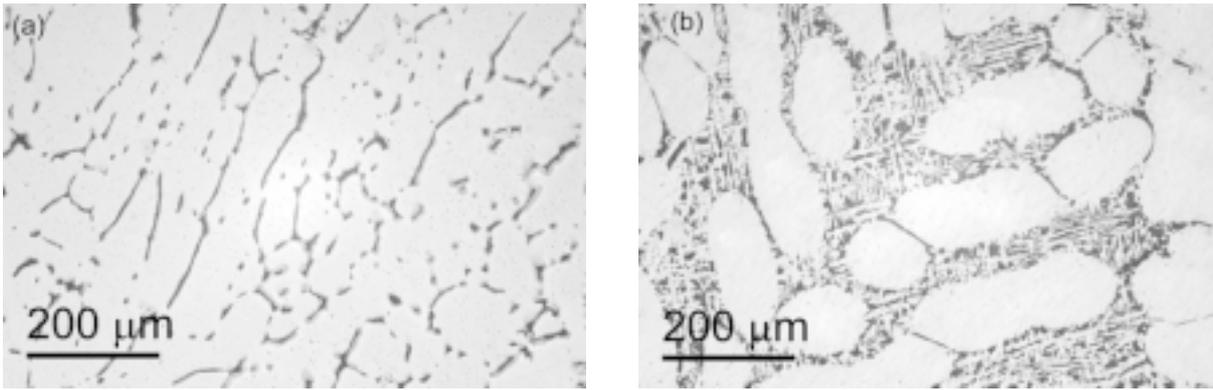

Fig. 4. Temperature dependence of the portion of completely wetted GBs in Zn – 6 wt.% Sn alloy.

3. RESULTS AND DISCUSSION

Optical micrographs of the Zn – 6 wt.% Sn polycrystals annealed at 290 °C and at 390 °C, 1 h are shown in Figs. 3a and 3b, respectively. Upon annealing at 390 °C (and at higher temperatures) GB wetting is clearly observed: the majority of GBs were wetted (see the light grey layers at the original GBs in Fig. 3b). Upon annealing at 290 °C only about 20% of the GBs are wetted (Fig. 3a). The fraction of wetted GBs in the Zn – 6 wt. % Sn polycrystals is shown as a function of the temperature in Fig. 4. Between 260 and 400 °C the fraction of the wetted GBs gradually increases with increasing tempera-

ture from 20 to 70 %. Therefore, the GB wetting phase transition proceeds in the Zn–Sn system. It starts below 260 °C, and even very close to the liquidus temperature the percentage of the wetted GBs does not reach 100% (Fig. 2). The tie-lines of the GB wetting phase transitions obtained in [15] for two individual [10$\bar{1}$0] tilt GBs with misorientation angles ϕ = 16° and 60° are also shown in Fig. 2 at T_{W1} = 386.5 °C and T_{W2} = 381 °C respectively. The comparison with Fig. 4 reveals, that both tilt GBs with low and high misorientation angles of 16° and 60° become wetted in the temperature interval when the majority (about 50 to 60%) of all GBs in a Zn–Sn polycrystal are already wetted. In [19, 20]

Fig. 5. Microstructure of the Zn – 5.3 wt.% In alloy after annealing at 275 °C, 1 h (a) and at 395 °C, 1 h (b) obtained by light microscopy. Zn-rich matrix appears white; GB wetting layers appear grey.
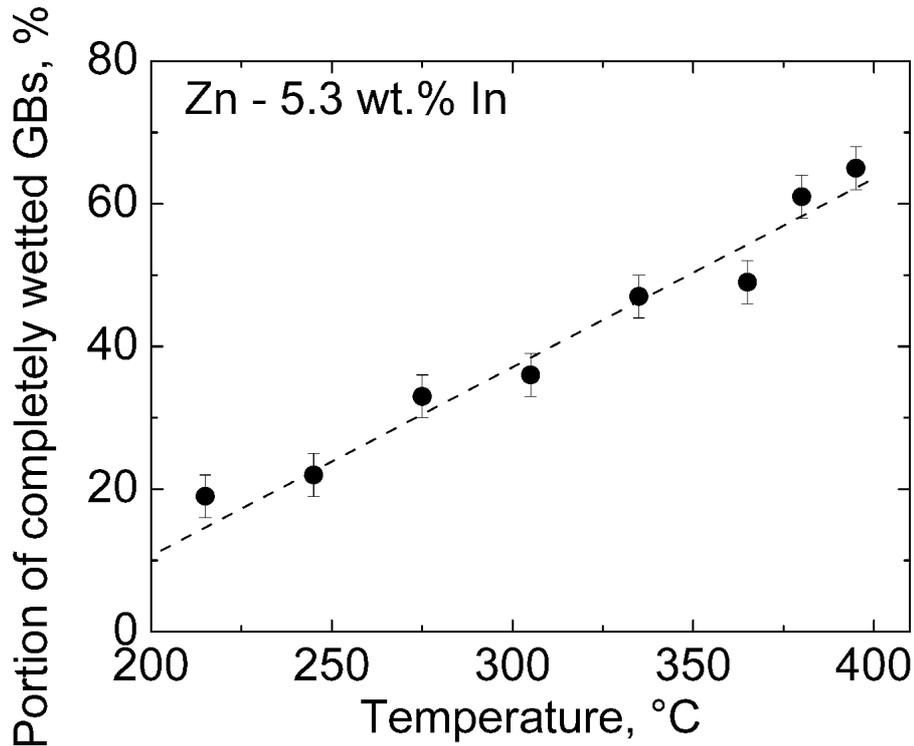

Fig. 6. Temperature dependence of the portion of completely wetted GBs in Zn – 5.3 wt.% In alloy.

the mean contact angle was measured in the Zn – 7 wt.% Sn polycrystals. It decreased with increasing temperature and reached zero at T_{w3} = 338 °C (see Fig. 2). In our samples only about 20% of all GBs are wetted at this temperature. The difference can be explained by the difference in chemical composition of alloys and in GB misorienation spectra (i.e. the polycrystals in this work contain most probably more low-energy GBs that those in Refs. 19, 20).

Optical micrographs of the Zn – 5.3 wt.% In polycrystals annealed at 275 °C and at 395 °C, 1 h are shown in Figs. 5a and 5b, respectively. Upon annealing at 395 °C GB wetting is clearly observed: the majority of GBs were wetted (see the light grey layers at the original GBs in Fig. 5b). Upon annealing at 275 °C only about 30% of the GBs are wetted (Fig. 5a). The fraction of wetted GBs in the Zn – 5.3 wt.% In polycrystals is shown as a function of the temperature in Fig. 6. Between 215 and 395 °C the fraction of the wetted GBs gradually increases with increasing temperature from 20 to 65 %. Therefore, the GB wetting phase transition proceeds in the Zn–In system. It starts below 215 °C, and even very
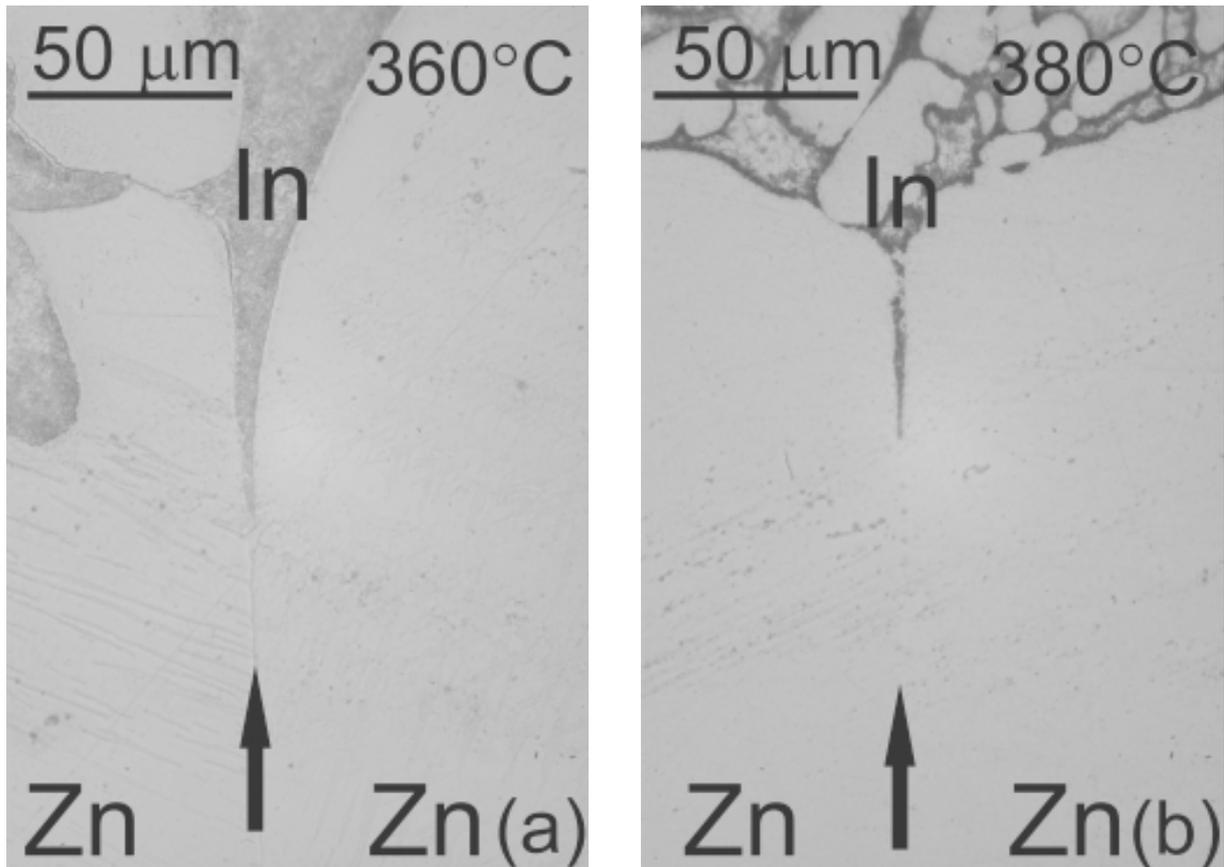
Fig. 7. Microstructure of the Zn bicrystal with [11$\overline{2}$0] ϕ = 79° tilt GB in Zn after annealing at 360 °C, 0.5 h (a) and 380 °C, 0.5 h (b) obtained by SEM (backscattered electrons). Zn-rich matrix appears white; GB wetting layers appear grey.

close to the liquidus temperature the percentage of the wetted GBs does not reach 100% (Fig. 1).

In Fig. 7 the contact angle θ formed by the In-containing melt at the [11$\overline{2}$0] ϕ = 79° tilt GB in Zn after annealing at 360 °C and 380 °C is shown as an example. The temperature dependences of the contact angles of all three GBs studied are shown in Figs. 8a and 8b. It can be clearly seen how the contact angle θ decreases with increasing temperatures, tends to zero at $T=T_w$ and remains zero at $T>T_w$. The temperatures T_w of the GB wetting transitions are T_{W1} = 362 °C, T_{W2} = 376 °C and T_{W3} = 375 °C for the [10$\overline{1}$0] tilt GBs with misorientation angles ϕ = 19° and 66° and the [11$\overline{2}$0] tilt GB with misorientation angle ϕ = 79°, respectively. The temperature dependences of contact angle intersect (at about 350 °C, Fig. 8b). Such pehomenon has been observed for the first time. The tie-lines of the GB wetting phase transitions at T_{W1} = 362 °C, T_{W2} = 376 °C, and T_{W3} = 375 °C obtained for the individual tilt GBs are also shown in Fig. 1. The comparison

with Fig. 6 reveals, that all three tilt GBs with low and high misorientation angles become wetted in the temperature interval when the majority (about 60%) of all GBs in a Zn–In polycrystal are already wetted. This fact and similar fact for the Zn–In system indicate that the whole energy spectrum for tilt GBs is rather narrow, and all GB energies of [11$\overline{2}$0] and [10$\overline{1}$0] tilt GBs are rather low in comparison with random GBs in a polycrystal.

All three $\theta(T)$ dependences in Fig. 8 are convex in the broad temperature interval below T_w. The convex shape and the break of the temperature derivative for $\theta(T)$ are usual for the GB wetting phase transformations [4–6,12–15]. However, the concave shape and the continuous temperature derivative for $\theta(T)$ were also recently observed for the first time [21]. Theory also predicts different critical exponents, namely 1/2 for the discontinuous and 3/2 for the continuous wetting transitions [22]. In Fig. 9 the measured $\theta(T)$ dependences (Fig. 8) are presented in the scaling coordinates log θ – log (($T - T_w$)/ T_w).
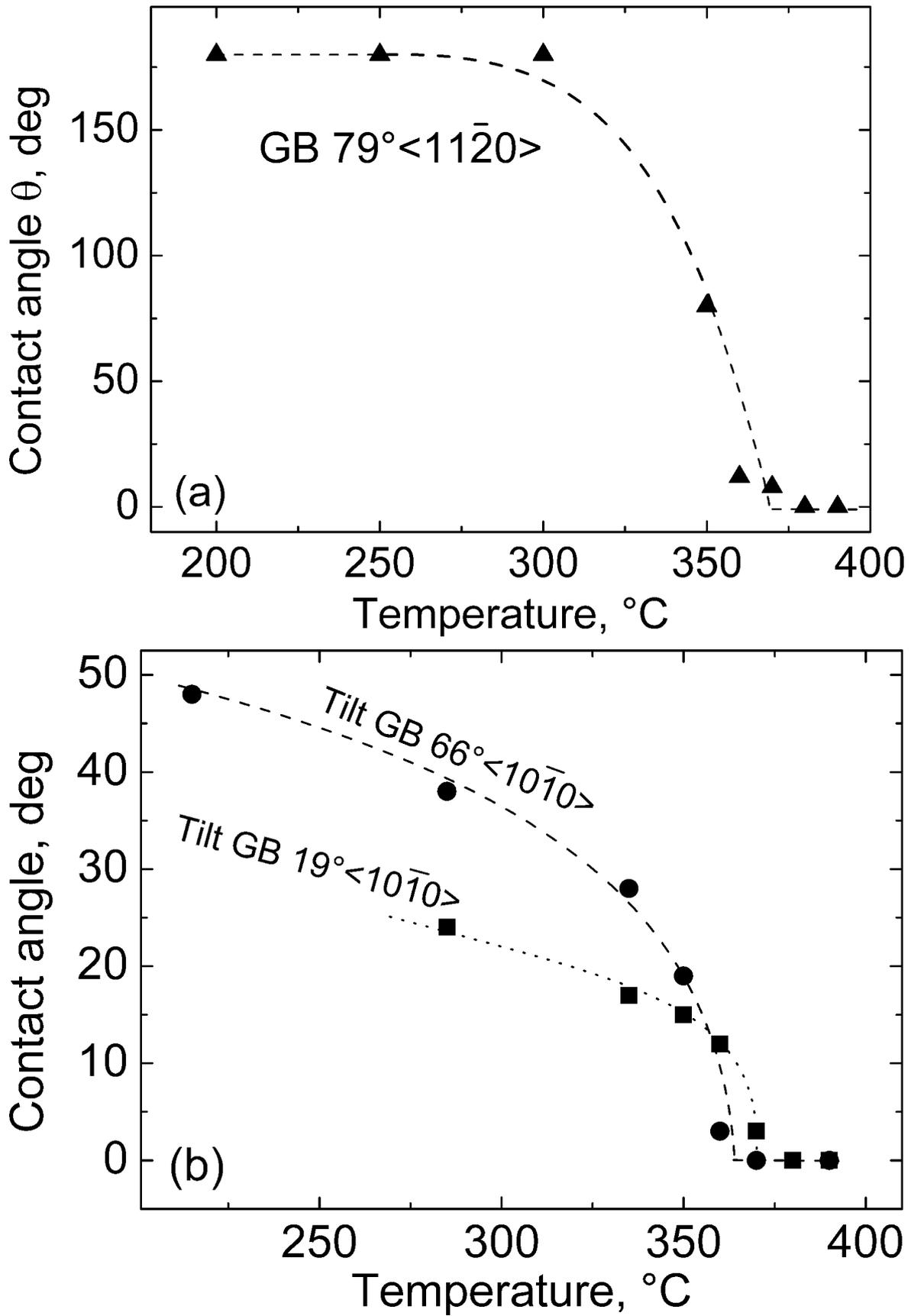
Fig. 8. Temperature dependences of the contact angle $\theta(T)$ for the $[11\bar{2}0]$ tilt GB with misorientation angle $\phi = 79°$ ($T_{W3} = 375$ °C) (a) and for the $[10\bar{1}0]$ tilt GBs with misorientation angles $\phi = 19°$ and $66°$ ($T_{W1} = 362$ °C, $T_{W2} = 376$ °C) (b).
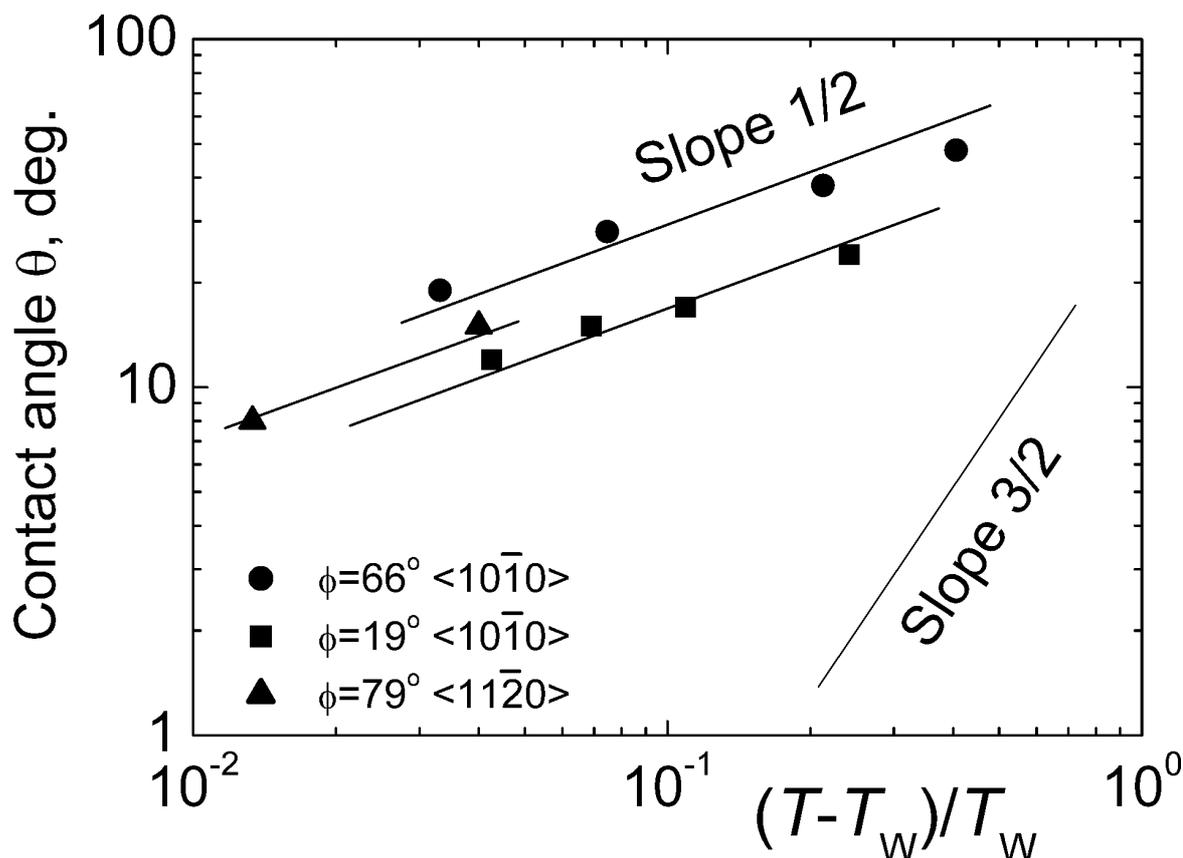
Fig. 9. Temperature dependences of the contact angle θ (same symbols as in Fig. 8) in scaling coordinates.

All data fit well to the slope 1/2. A line with the slope 3/2 is also shown for the comparison. In other words, the scaling condition for the discontinuous transition is fulfilled for the wetting of Zn GBs by the In-rich melt. The scaling exponent of 1/2 for GB wetting transition was also observed for tilt Al GBs wetted by the Sn-rich melt [5].

4. CONCLUSIONS

The wetting phase transition of grain boundaries (GBs) by the melt proceeds in the Zn–Sn and Zn–In systems. In the Zn – 6 wt.% Sn polycrystals, the fraction of the completely wetted GBs gradually increases from 20 to 70% with increasing temperature between 260 and 400°C. In the Zn – 5.3 wt.% In polycrystals, the fraction of the completely wetted GBs gradually increases from 20 to 65% with increasing temperature between 215 and 395 °C. The contact angle θ for bicrystals decreases with increasing T and reaches zero (complete wetting) at a certain temperature T_w. The temperatures T_w of the GB wetting transitions are T_{W1} = 362 °C, T_{W2} =

376 °C, and T_{W3} = 375 °C for the [10$\bar{1}$0] tilt GBs with misorientation angles ϕ = 19° and 66° and the [11$\bar{2}$0] tilt GB with misorientation angle ϕ = 79°, respectively. Tilt GBs in Zn–Sn and Zn–In systems become completely wetted when about 60-70% of GBs with higher energy are already completely wetted in a polycrystal. Similar fact was observed also for tilt GBs in Al wetted by the Zn-rich melt. It means that the plain matching in tilt GBs ensure them a rather low energy independently on their misorientation.

REFERENCES

[1] J.W.Cahn // *J. Chem. Phys.* **66** (1977) 3667.

[2] C. Ebner and W.F. Saam // *Phys. Rev. Lett.* **38** (1977) 1486.

[3] N. Eustathopoulos // *Int. Met. Rev.* **28** (1983) 189.

[4] B. Straumal, T. Muschik, W. Gust and B. Predel // *Acta Metall. Mater*. **40** (1992) 939.

[5] B. Straumal, D. Molodov and W. Gust // *J. Phase Equilibria* **15** (1994) 386.

[6] B. B. Straumal, *Grain Boundary Phase Transitions* (Nauka publishers, Moscow, 2003), In Russian.

[7] S.H. Islam, X. Qu and X. He // *Powder Metal*. **50** (2007) 11.

[8] D.Q. Wei, Q.C. Meng and D.C. Jia // *Ceram. Internat.* **33** (2007) 221.

[9] K.P. Solek, R.M. Kuziak and M. Karbowniczek // *Arch. Metall. Mater.* **52** (2007) 25.

[10] Z.S. Ji, M.L. Hu and X.P. Zheng // *J. Mater. Sci. Technol*. **23** (2007) 247.

[11] Y.A. Shatilla and E.P. Loewen // *Nuclear Technol.* **151** (2005) 239.

[12] B.B. Straumal and W. Gust // *Mater. Sci. Forum* **207-209** (1996) 59.

[13] B. Straumal, V. Semenov, V. Glebovsky and W. Gust // *Defect Diff. Forum* **143-147** (1997) 1517.

[14] L.-S. Chang, E. Rabkin, B.B. Straumal, S. Hofmann, B. Baretzky and W. Gust // *Defect Diff. Forum* **156** (1998) 135.

[15] B. Straumal, W. Gust and T. Watanabe // *Mater. Sci. Forum* **294-296** (1999) 411.

[16] *Binary Alloy Phase Diagrams*, ed. by T.B. Massalski (ASM International, Materials Park, Ohio, 1990).

[17] O.A. Kogtenkova, B.B. Straumal, S.G. Protasova and P. Zięba // *Def. Diff. Forum* **237–240** (2005) 603.

[18] B.B. Straumal, V.G. Sursaeva and A.S. Gornakova // *Zt. Metallkd*. **96** (2005) 1147.

[19] A. Passerone, N. Eustathopoulos and P. Desre // *J. Less-Common Metals* **52** (1977) 37.

[20] W.A. Miller and W.M. Williams // *Can. Metall. Quat.* **2** (1963) 57.

[21] B.B. Straumal, A.S. Gornakova, O.A. Kogtenkova, S.G. Protasova, V.G. Sursaeva and B. Baretzky // *Phys. Rev. B* **78** (2008) 054202.

[22] S. Dietrich, *Phase Transitions and Critical Phenomena* vol. 12, ed. by C. Domb and J.L. Lebowitz (Academic Press, London, 1988).