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# Direct observation of strain-induced non-equilibrium grain boundaries

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ABSTRACT

The grain boundary (GB) wetting by the melt and second solid phase has been studied in the Sn–Pb system both in equilibrium conditions and during continuous strain. The percentage of Sn/Sn GBs completely wetted by the melt increases from 80% at eutectic temperature $T_e = 183$ °C to 100% at 220 °C. The percentage of Pb/Pb GBs completely wetted by the melt increases from 0% at $T_e$ to 100% at 270 °C. Below $T_e$ only incomplete wetting of Pb/Pb GBs by solid Sn and Sn/Sn GBs by solid Pb has been observed after long annealing. However, during strain the lattice dislocations are continuously absorbed by GBs increasing the GB energy. As a result, the complete wetting of such non-equlibrium Sn/Sn GBs by the second solid phase Pb appears. Therefore, the difference in energies between equilibrium and non-equilibrium grain boundaries has been experimentally demonstrated for the first time.

## 1. Introduction

The grain boundary (GB) wetting by the melt and by the second solid phase is not only the interesting and technologically important phenomenon. It can be also used as an instrument to characterize the difference between GB energies in various processes. The difference between equlibrium and non-equlibrium GBs has been directly observed by TEM already in 1970s [1]. Pumphrey and Gleiter observed how the lattice dislocations are absorbed by the Ni – 5 wt% Al GBs at room temperature and delocalized and relaxed in GB by *in situ* heating up to 300 °C [1]. Later the idea of non-equlibrium GB has been extensively used in order to describe the unique properties of nanograined materials manufactured by the severe plastic deformation (SPD) [2,3]. The idea of SPD is to deform the material in a confined space. It permits to increase the strain up to enormous values without fracture of a material. From the thermodynamic point of view, the difference between equlibrium and non-equlibrium GBs is that the non-equlibrium ones have higher energy. However, the direct experimental evidence of this fact has been never obtained up to now. It is a main goal of this work.

## 2. Experimental

In this work, the Sn–Pb alloys with tin concentrations of 6, 10, 18, and 95 wt% were studied (see phase diagram in Fig. 1) [4]. They were prepared by means of melting in vacuum from extremely pure components (99.9995 wt% Sn and 99.9993 wt% Pb). The resulting ingots with a diameter of 10 mm were cut into 2 mm thick disks, which were chemically polished and were then sealed into evacuated (a residual pressure of $4 \times 10^{-4}$ Pa) Pyrex glass ampoules. After that, the ampoules were annealed in a muffle furnace at temperatures of 130–310 °C for 2–1500 h. Experimental points corresponding to studied temperatures and concentrations are shown in the phase diagram of the Sn–Pb system (Fig. 1). After annealing, the samples were quenched in water, ground, polished, and analyzed by means of scanning electron microscopy on a Tescan Vega NS5130MM instrument equipped with the LINK energy-dispersive spectrometer produced by Oxford Instruments. 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 was performed adopting the following criterion: every boundary between Sn or Pb grains was considered to be completely wetted by the melt or second solid phase phase only when a macroscopic layer of the melt or second solid phase can be observed by SEM; if such a layer appeared to be interrupted, the GB was regarded as incompletely wetted. The contact angles $\theta$ were measured simultaneously for all

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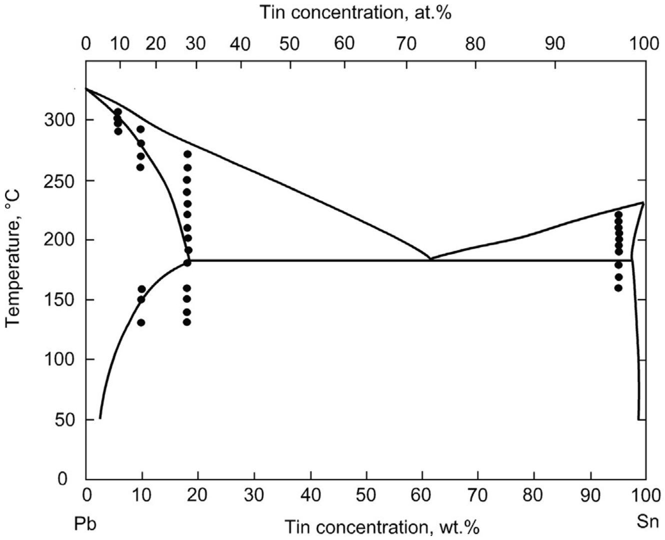

**Fig. 1.** (a) Pb–Sn phase diagram [4]. Filled circles show temperatures of annealings.

GBs. For the GBs completely covered by a liquid phase the $\theta=0°$ value was assigned. At least 300 GBs were analyzed at each temperature. Typical micrographs obtained by SEM are shown in Fig. 2. The *in situ* investigation of the microstructure of Sn–Pb under continuous strain has been performed in the installation for internal rupture described in details in [5–9]. Bimetallic solid phase joints (Sn/Pb) with atomically clean interfaces were used as a macroscopic model of the deformed GBs.

## 3. Results and discussion

The GB phase transformations can drastically modify the properties of polycrystals [10,11]. Most important GB phase transformation is the transition from incomplete to complete wetting of a GB by a second phase. The wetting phase can be either liquid or solid. In case of incomplete wetting the contact angle between second phase and GB is non-zero $\theta > 0°$, and the wetting phase forms the lenticular particles separated by the “dry” GB portions. It is because the enthalpy of a GB unit area $\sigma_{GB}$ is lower than that of two interphase boundaries $\sigma_{IB}$, namely $\sigma_{GB} < 2\ \sigma_{IB}$. In case of complete wetting $\sigma_{GB} > 2\ \sigma_{IB}$, $\theta=0°$, and a layer of wetting phase completely substitutes a GB [9,12]. The transition from incomplete to complete wetting of a GB by a liquid phase (melt) at a certain temperature $T_w$ is described by a horizontal tie-line in the two-phase “solid solution+liquid” area of a bulk phase diagram [13,14]. Such tie-line connects the points at solidus and liquidus lines at $T_w$.

Fig. 2 shows the micrographs of the microstruture of Sn–Pb alloys annealed at various temperatures and strained *in situ*. Sn-rich areas appear dark, Pb-rich areas appear bright. In Fig. 2a the structure of Sn – 5 wt% Pb alloy annealed at 190 °C above eutectic temperature $T_e=183$ °C is shown. The majority of Sn/Sn GBs is completely wetted by the Pb-rich melt. In other words, Pb-rich melt forms the continous layer between two neighboring Sn grains. The minority of Sn/Sn GBs is incompletely wetted by the Pb-rich melt. In this case the layer of Pb-rich melt between two neighboring Sn grains is interrupted. By the increase of temperature the percentage of Sn/Sn GBs completely wetted by the Pb-rich melt increases (Fig. 3). It increases from 80% at eutectic temperature $T_e$ (when the melt appears in the system) to 100% at 220 °C (see micrograph in Fig. 2b). Below $T_e$ only incomplete wetting of Sn/Sn GBs by solid Pb has been observed after long annealing (Fig. 2c). The transition from incomplete to complete GB wetting proceed also in the Pb-rich alloys (Fig. 3). The percentage of Pb/Pb GBs completely wetted by the melt increases from 0% at $T_e$ to 100% at 270 °C (Fig. 2d). Below only incomplete wetting of Pb/Pb GBs by solid Sn has been observed (Fig. 2e), similar to the Sn-rich alloys.

During straining, the lattice dislocations are continuously absorbed by GBs increasing the GB energy [1]. The condition of incomplete GB wetting is $\sigma_{GB} < 2\ \sigma_{IB}$. If the GB energy $\sigma_{GB}$ increases due to the absorption of dislocations, the transition to the condition $\sigma_{GB} > 2\ \sigma_{IB}$, can take place and the GBs with zero contact angle $\theta=0°$ and continuous layers can appear in the alloy. The Sn-grains completely surrounded by the lead-rich layers appear indeed by continous straining the eutectic alloy Pb – 62 wt% Sn *in situ* at 300 K (Fig. 2f). It means that the complete wetting of such non-equlibrium GBs by the second solid phase takes place instead of the partial GB wetting in the equilibrium annealings. Therefore, the difference in energies between equilibrium and non-equilibrium grain boundaries has been experimentally demonstrated for the first time.

## 4. Conclusions

The grain boundary (GB) wetting by the melt and second solid phase has been studied in the Sn–Pb system both in equilibrium conditions and during continuous strain. Above eutectic temperature $T_e$ GBs both completely and incompletely wetted by the melt exist. Below $T_e$ only incomplete wetting of Pb/Pb GBs by solid Sn and Sn/Sn GBs by solid Pb has been observed after long annealing. However, during strain the lattice dislocations are continuously absorbed by GBs increasing the GB energy. As a result, the complete wetting of such non-equlibrium Sn/Sn GBs by the second solid phase Pb appears. Therefore, the difference in energies between equilibrium and non-equilibrium grain boundaries has been experimentally demonstrated for the first time.

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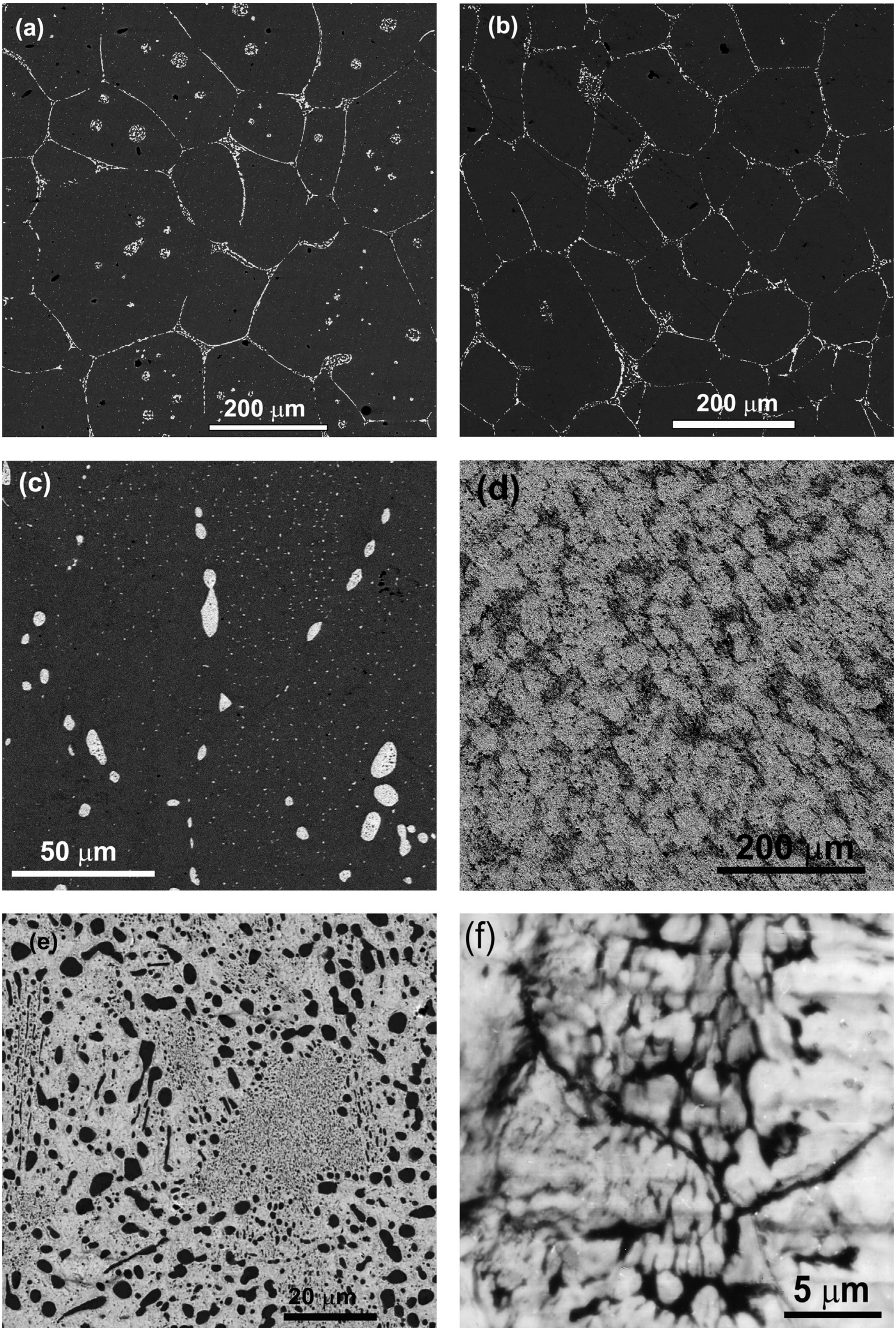

**Fig. 2.** Micrographs showing the microstruture of Sn–Pb alloys annealed at various temperatures and strained *in situ*. Sn-rich areas appear dark, Pb-rich areas appear bright. (a, b) Sn – 5 wt% Pb alloy annealed at 190 (a) and 215 °C (b) above $T_e = 183$ °C. (c) Sn – 5 wt% Pb alloy annealed at 170 °C below $T_e$. (d) Pb – 18 wt% Sn alloy annealed at 270 °C above $T_e$. (e) Pb – 18 wt% Pb alloy annealed at 170 °C below $T_e$. (f) Pb – 62 wt% Sn alloy continuously strained *in situ* at room temperature.

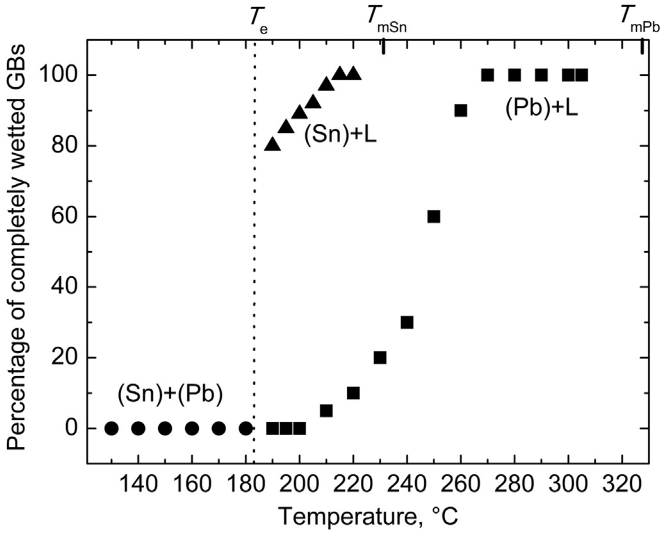

**Fig. 3.** Temperature dependence of percentage of completely wetted GBs. Filled triangles: wetting of Sn/Sn GBs by the melt. Filled squares: wetting of Pb/Pb GBs by the melt. Filled circles: wetting of Pb/Pb GBs by the solid Sn and of Sn/Sn GBs by the solid Pb.

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