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PROPERTIES OF TILT BOUNDARIES <001> IN TIN AND TIN-SODIUM ALLOYS IN THE VICINITY OF THE SPECIAL BOUNDARY - GENERAL BOUNDARY TRANSFORMATION

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Abstract

A relative surface tension of tilt boundaries in tin near the coincidence misorientation $\Sigma 17$ has been determined from the form of triple junctions of tin threecrystals. The study of these boundaries migration has shown that at a certain temperature, T_c, they loose their special properties and become general-type boundaries. Also the temperature dependence of the surface tension exhibits a bending at T_c. The dependence of T_c on the misorientation angle φ around the <001> axis and on the additional misorientation angles /components of twist and "second tilt"/ for a fixed φ have been plotted. The results are attributed to delocalisation of secondary grain boundary dislocations at the grain boundary dislocations at the grain boundary phase transition. The effect of substitutional impurity on T_c at a fixed φ has been studied.

Introduction

In papers 1,3 the change of thermodynamic (energy) and kinetic (mobility) properties of single tilt boundaries in tin within the angle interval pear the Σ 17 special misorientation ($\varphi = 28.07^{\circ}$) has been explained as a phase transition from special boundary to general one.

The presence of impurities can materially alter the behaviour of such grain boundary phase transition.

The aim of this study is to investigate the effect of impurities on the special-to-general boundary phase transition for the $\langle 001 \rangle$ tilt boundaries in the tin-sodium system.

2. Experimental

Sodium was chosen as impurity for the tin on which our previous experiments [1] has been carried out. Sodium dissolves in tin forming a solid solution to a concentration of 0.48 weight % (2.4at%) [4] . The impurity was introduced into the tin of a nominal purity of 99.8888% Sn. The maximum concentration of sodium in the Sn-Na alloys under study was $\sim 1.10^{-1}$ at%. The four other alloys with lower concentration of sodium were produced by successive dilution. The minimum concentration of sodium in the alloys came to $1 \cdot 10^{-4}$ at%. The impurity content was controlled by mass-spectrometric analysis.

The ratio of the special boundary surface tension to that of general boundary, σ_{sp}/σ_{g} , was studied by the triple junction shape. The triple junction is formed by a boundary with the misorientation angle $\varphi_1 = 28.3^{\circ}$ near the special angle $\varphi_s = 28.07$ (Σ 17) and by two general boundaries with the angle φ determined by the relationship $\varphi_2 = \varphi_3 = (90 - \varphi_1)/2 = 30.9^{\circ}$ and situating far from the region of the existence of the Σ 17 special boundary.

The triple junction specimens were grown by the technique of directed crystallisation in an atmosphere of high-purity argon in ultra-pure graphite crucible. The specimen containing triple junction was out of the tricrystal, chemically polished in a mixture of HNO_3-40%HF and then placed into a high-temperature attachment to an optical microscope. Anneals were carried out in the HP argon, the temperature was maintained with an accuracy to $\pm 0.3^{\circ}$. At successive anneals the triple junction shifted. Since $\sigma_2 = \sigma_3 = \sigma_g$, the special boundary with $\sigma_1 = \sigma_s$ remained flat all the time. The triple junction vertex angle was measured after energy anneal. Quantities h and l have to be determined (see Fig. 1b). In this case $\sigma_s/\sigma_g = \sigma_1/\sigma_2 = 2\cos[\operatorname{atan}(l/2h)]$. The magnification was chosen so that the measurements of h and l were carried out in the vicinity of the junction, where the boundaries with

σ_2 and σ_3 had been rectilinear, and the ratio l/a does not exceed 0.1. It has been shown experimentally in paper [1] that by this technique we can measure the equilibrium value of the triple junction vertex angle.

3. Results and discussion

The temperature dependences of σ_s/σ_g in the Sn-Na system has been studied for 5 alloys of the following concentrations: 1.10^{-4}; 1.10^{-3}; 1.10^{-2}; 3.10^{-2}; 1.10^{-1} at%Na and for the misorientation angle $\varphi = 28.3^{\circ}$ at temperatures from $0.85\ T_m$ to T_m.

The error of the mass-spectrometric analysis was $\pm 1.10^{-3}$ at%. The concentration of Na in the most diluted specimen is assumed to be $1 \cdot 10^{-4}$at% Na proceeding from the technique of its production by successive dilution and subsequent recrystallisation in the Ar atmosphere.

Fig. 1 illustrates the temperature dependences of the ratio σ_i/σ_g . The curves are arranged in order of increasing concentration of Na in the alloys. Near some temperature T_c the ratio σ_i/σ_g begins to grow, at T_c it reaches its maximum and after that falls down. The temperature decreases from specimen to specimen as the sodium concentration in alloys is increased. The position of breaks in the temperature curves of σ_i/σ_g does not depend on the driving force of the junction displacement, the sequence of the measurements and the misorientation angles of general grain boundaries in the junction [1] . Thus the position of breaks in the temperature dependences of only is determined by the impurity concentration and within the limits of experimental error is independent of the other factors. Earlier [1] we have observed similar features in the temperature dependences of the surface tension ratio σ_s/σ_g .

Fig. 2 illustrates the break temperature T_c as a logarithmic function of Na concentration for 5 Sn-Na alloys. As seen, with increasing content of sodium in alloys the temperature T_c drops down.

If the surface tension temperature dependences $\sigma_s(T)$ and $\sigma_g(T)$ meet below the melting temperature, this is indicative of the transformation from the special to the general boundary. At the first-kind phase transition the surface tension temperature dependences $\sigma(T)$ should exhibit a break. Moreover, in the material with impurities the entropy of boundaries is higher and the surface tension lower than in the pure material. If the general boundary surface tension decreases with increasing impurity concentration to much lower extent than that of special boundary, the temperature T_{c2} , at

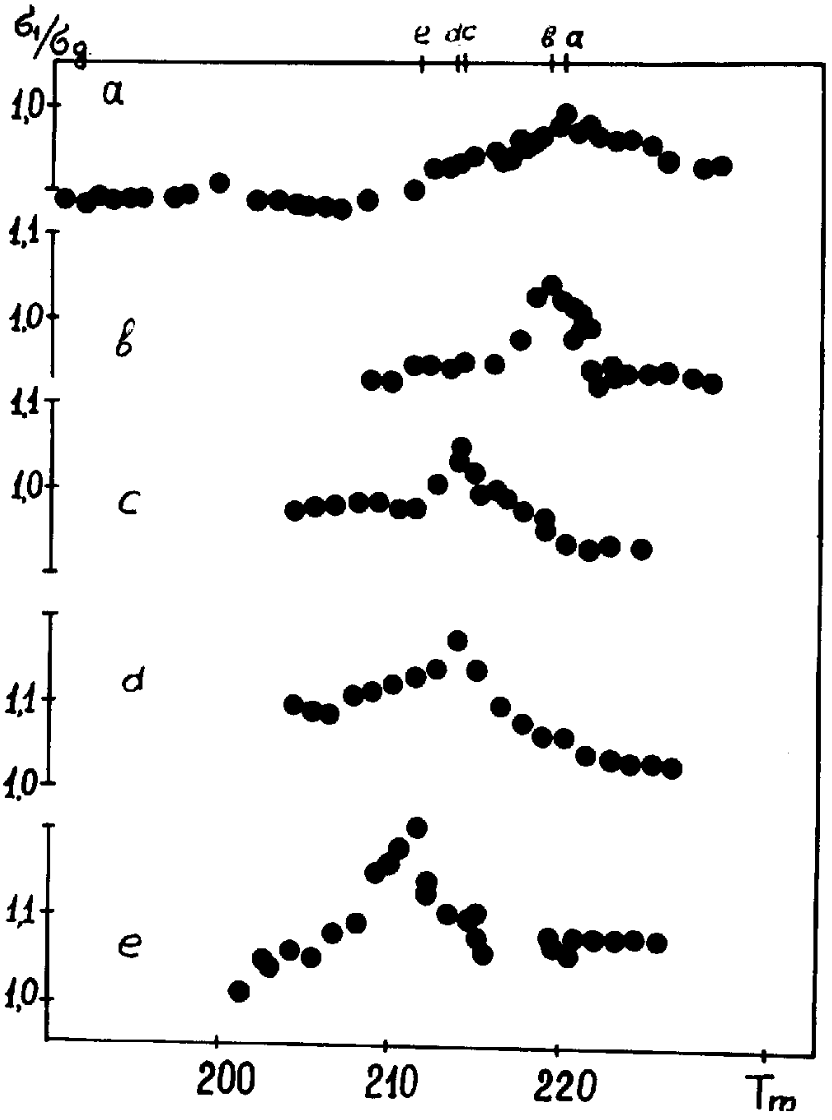

Figure 1. Temperature dependences of the ratio of the special boundary tension $\sigma_1 = \sigma_s$ to the general boundary tension $\sigma_2 = \sigma_3 = \sigma_g$ for alloys of following concentrations: a) $1 \cdot 10^{-4}$ at% Na; b) $1 \cdot 10^{-3}$ at% Na; c) $1 \cdot 10^{-2}$ at% Na; d) $3 \cdot 10^{-2}$ at% Na; e) $1 \cdot 10^{-1}$ at% Na.

which the structure of general boundary becomes energetically favourable, decreases as compared with T_{c1} for pure material ($T_{c1} > T_{c2}$, Fig. 4).

The shape of curves in Fig. 2 allows us to speak about breaks in the $\sigma_s/\sigma_g(T)$ dependences. Fig. 3 shows how decreases with increasing impurity concentration. All this along with our precious results [1], enables us to suppose that at temperatures T_i a phase transition from special to general grain boundary takes place. Judging by appearances of the surface tension temperature dependences, this is a first-kind phase transition.

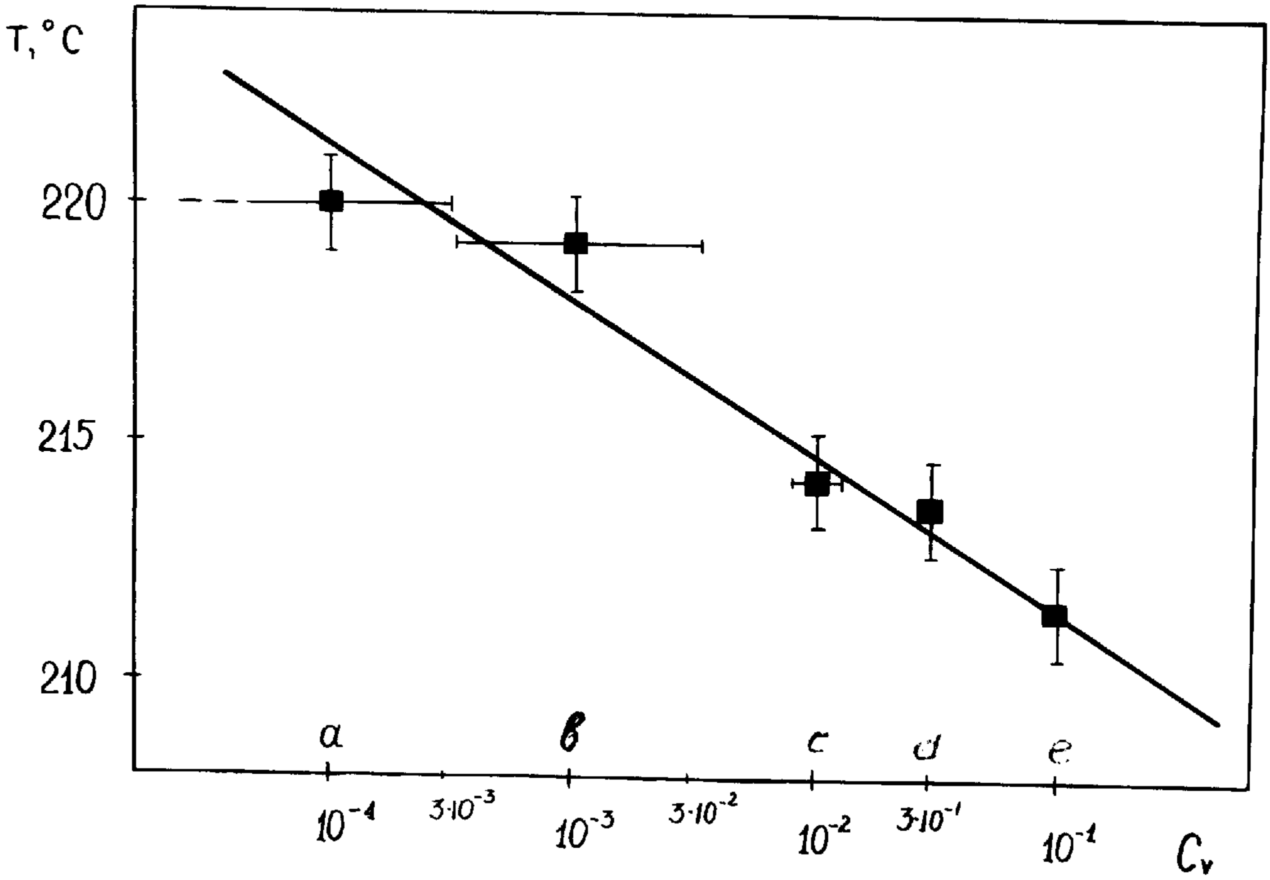

Figure 2. The dependence of break temperature on sodium concentration in the alloys studied.

From Gibbs adsorption equations [4] and condition of thermodynamic equilibrium we obtain

$$dT \simeq RT\frac{N_s' A_g - N_g' A_s}{S_g' A_s - S_s A_g}\, d\ln C - RT\frac{N_s A_g - N_g A_s}{S_g' A_s - S_s' A_g}\, dC \qquad (1)$$

The whole area variation does not exceed several percents, therefore we assume further that $A_g = A_s = A$

Then Eqn. (3) takes the form

$$dT \simeq RT\frac{N_s' - N_g'}{S_g' - S_s'}\,d\ln C - RT\frac{N_s - N_g}{S_g' - S_s}\,dC \qquad (2)$$

The differences between surface excesses in the numerator and denominator of expression (4) coincide with those of boundary concentrations and entropies.

For a pure material $S_g' - S_s' = q_{tr}/T$, where q_{tr} is the grain boundary phase transition heat. For a solution the first nondisappearing correction to this quantity is linear with respect to N_s' and N_g', therefore for the adsorption values of the order of some percents this correction can be neglected. Let us consider some limiting cases:

1. Both grain boundary solutions are infinitely diluted. Then $\Gamma_{s,g} = j_{s,g}C$ + the terms of the higher orders with respect to C, where Γ is the grain boundary adsorption; j_s, j_g are adsorption constants. The form Eqn. (4) we have

$$\Delta T \simeq \frac{RT^2}{q_{tr}}\left(j_s - j_g - N_s + N_g\right)\Delta C$$

The order of magnitude of q_{tr} is assumed to be equal to the tin melting heat: $q_{tr} \simeq 7.1\ KJ/mol$ [5].

2. Both grain boundary solutions are saturated:

$N_s' = \text{const}$; $N_g' = \text{const}$.

Taking into account that at low concentrations $|C| \ll |\ln C|$, we obtain

$$\Delta T \simeq \frac{RT^2}{q_{tr}}\left(N_s' - N_g'\right)\Delta \ln C$$

This fits the experimental dependence $\Delta T(C)$ (Fig. 1). In this case $N_g' - N_s' \simeq 5\ 10^{-3}$ i.e. the absolute difference between the number of adsorption sites in the general and special boundaries comes to ~ 0.5% of the total number of sites in a boundary.

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