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Deformation-Induced Phase Separation

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Deformation may change not only the structure of the alloy but also the phase state and spatial distribution of components. Plastic deformation of tin–lead solder within the broad range of deformation rates does not form the metastable solutions but, instead, accelerates the decomposition of supersaturated (quenched) solid solutions. Creep of such solder leads to spatial separation of phases ('squeezing' of tin).

Деформація може змінювати не тільки структуру стопу, але також фазовий стан і просторовий розподіл компонентів. Пластична деформація олов'яно-свинцевої люти в широкій області швидкостей деформації не створює метастабільний стан, але, замість цього, прискорює розпад перенасичених (загартованих) твердих розчинів. Плазучість цієї люти призводить до просторового поділу фаз («видавлювання» олова).

Деформация может изменять не только структуру сплава, но также фазовое состояние и пространственное распределение компонентов. Пластическая деформация оловянно-свинцового припоя в широкой области скоростей деформации не образует метастабильное состояние, но, вместо этого, ускоряет распад перенасыщенных (закалённых) твёрдых растворов. Ползучесть этого припоя приводит к пространственному разделению фаз («отжатие» олова).

Key words: solid solution, decomposition, two-phase alloy, plastic deformation, creep.

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1. INTRODUCTION

Influence of deformation on the phase transformations involving separation of phases is studied for many years. Yet, so far, there is no clear understanding of these phenomena. In a given work, we consider two kinds of phase separation: decomposition of solid solution under fast or slow plastic deformation and spatial separation of already existing phases under creep in multiphase alloys.

Actually, deformation can lead to two competing effects of opposite directions. On the one hand, steady deformation process generates the thermally non-activated atomic displacements ('ballistic jumps' as called by George Martin, Bellon Pascal and others [1, 2]). Clearly, such ballistic jumps do not obey the thermodynamics of equilibrium systems; therefore, one should expect the shifts of equilibria lines on the phase diagrams. Thus, one might expect that deformation can form the metastable solid solutions beyond the solubility limits. On the other hand, deformation practically always generates the excess vacancies and therefore should lead to acceleration of all diffusion-controlled processes, and, in particular, to acceleration of diffusional decomposition. In this study, we consider this second possibility.

Decomposition of solid solutions induced by plastic deformation was observed in [3]. It is already known that plastic deformation accelerates the diffusion, and anomalous mass transfer is observed across the interface [4, 5]. Anomalous mass transfer (if any) and formation of metastable solutions under plastic deformation are, most probably, interrelated. To observe the maximal possible extent of metastable phase formation, fast transfer and also as large contact zone as possible are necessary.

2. DEFORMATION-INDUCED DECOMPOSITION

Well-known alloy Pb–62% Sn forms eutectic, which can be considered as the widespread interface between tin-based (β-phase) and lead-based (α-phase) phases. In this eutectic content of tin in α-phase is 24 at.% at temperature 183°C, and that at room temperature is 3 at.%. Our aim is to study the influence of deformation magnitude and rate on the phase content and structure. The XRD study is performed by diffractometer (Fig. 1, FeK_α-radiation) and by Debye–Scherrer camera (Fig. 2, CuK_α-radiation).

Concentration of tin in α-phase (c_0) was determined according to modified composition dependence of the lattice constant:

$$a_0 = 4.9508 - 0.00135c_0 \text{ (Å)}.$$

Samples were quenched with the cooling rate of about 2000 K/s from

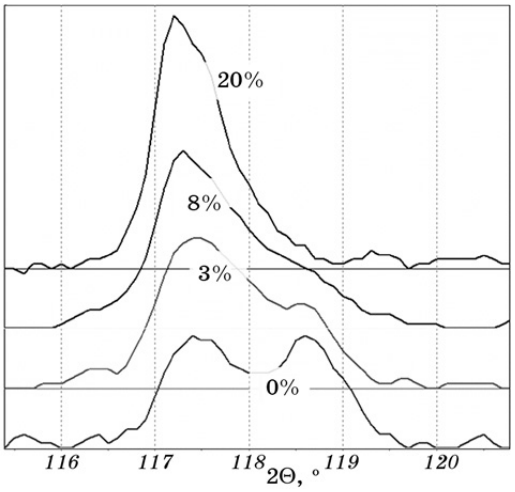

Fig. 1. Profiles of (331) line for α-phase of the quenched alloy Pb–62% Sn after deformation.

175°C. In this case, phase partially decomposed, and profiles of Bragg peaks became bimodal. One of the modes corresponded to initial composition, and another one corresponded to equilibrium concentration of tin at 20°C in the solid solution. Values of tin concentrations corresponding to two modes are presented in Table 1.

No intermediate compositions were observed: initial peak shrinked and peak of equilibrium composition grew instead (see Fig. 1).

To take into account the natural ageing, decomposition kinetics of α-phase at 25°C was investigated (Fig. 3). One can see that, within the first one hour, a structure is not changed significantly.

We investigated influence of deformation at various magnitudes and rates.

Main results

1. Plastic deformation induces decomposition of lead-based solid solu-

TABLE 1.

Deformation, %	First component c_{Sn}, at.%	Second component c_{Sn}, at.%
0	5.5	28.0
3	4.9	26.8
8	3.4	24.9
20	2.8	22.6

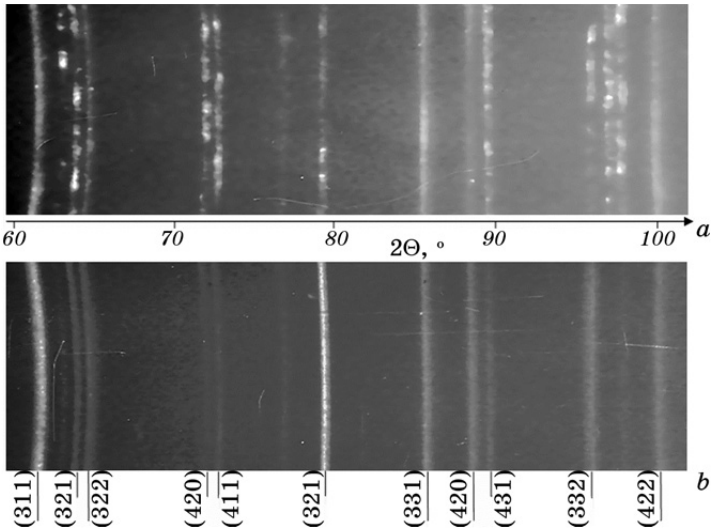

Fig. 2. Debye patterns of Pb–Sn alloy just after quenching (*a*) and after plastic deformation by 30% (*b*).

tion with formation of almost pure lead. Extent of decomposition (see Fig. 4) linearly depends on the total deformation magnitude (until the moment of full decomposition).

2. Extent of decomposition does not depend on the deformation rate at fixed deformation magnitude, at least within rates interval $5 \cdot 10^{3}$–$5 \cdot 10^{-4}$ s^{-1}.

3. Extent of decomposition does not depend on the history of defor-

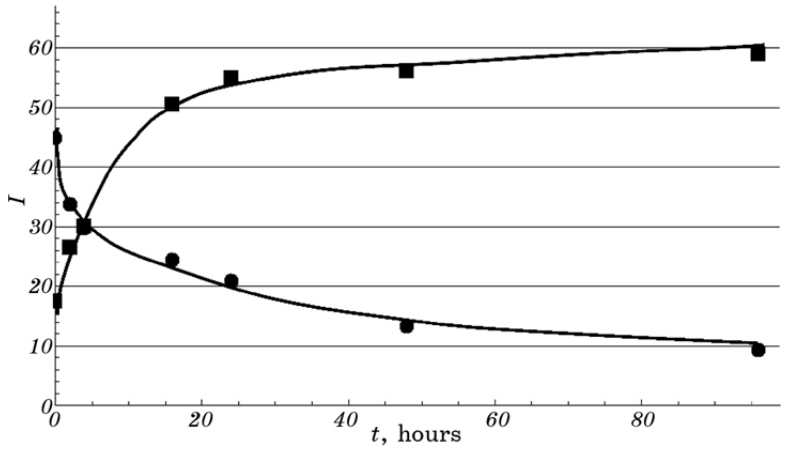

Fig. 3. Time dependences of two modes intensity of the (421)-line of α-phase at 25°C natural ageing (■—new structure mode, •—old structure mode).

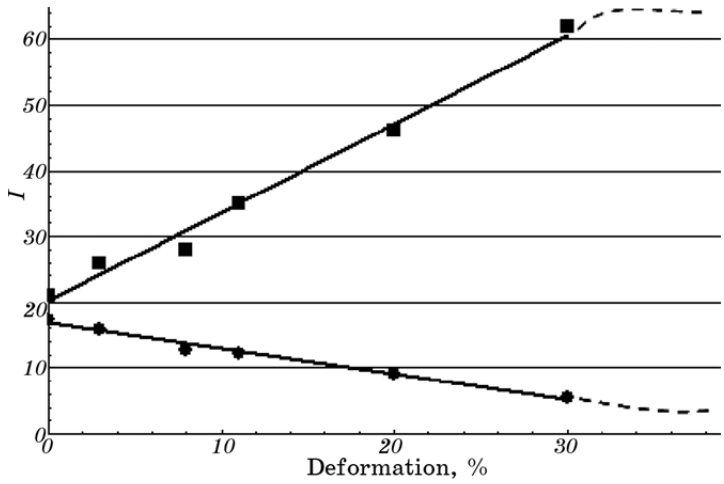

Fig. 4. Deformation magnitude dependences of two modes intensity of the (421)-line of α-phase at 25°C (■—new structure mode, •—old structure mode).

mation (single stage, two-stage, three stages, …), but only on eventual deformation.

4. In the quenched sample, the tin crystallites (β-phase) have much greater size than those of α-phase. Deformation leads to refinement of grains (see Fig. 2).

Naive model of the above-mentioned results can be suggested, based on the analysis of extra vacancies generation proportional to the velocity and density of dislocations and vacancy relaxation proportional to the magnitude of vacancy supersaturation:

$$\frac{dC_V}{dt} = A\frac{d\varepsilon}{dt} - \frac{C_V - C_V^{eq}}{\tau_V}. \tag{1}$$

Here, vacancy generation rate coefficient A can be estimated from elementary picture of vacancy generation by moving dislocations [6, 7] (Hirsch, Mott, Nabarro *et al.*):

$$A = \frac{b}{2}(f\varsigma\rho_s)^{1/2}, \tag{2}$$

where b is a Burgers vector magnitude, $\varsigma \approx 0.5$ is the fraction of forest dislocations, $\rho_s \approx \rho_e = \rho/2$ is the density of screw dislocations, ρ is the total dislocation density, f is the fraction of vacancy producing jogs on a gliding screw.

In the steady-state regime,

$$C_V = C_V^{eq} + \tau_V A\,(d\varepsilon/dt). \tag{3}$$

If $\tau_V A(d\varepsilon / dt) >> C_V^{eq}$ (and estimations according to Eq. (2) show that such situation is quite possible), then vacancy concentration and, accordingly, diffusivity are proportional to the deformation rate.

In case of cellular decomposition the growth of transformed region proceeds, in average, with constant velocity, proportional to diffusivity in the moving interface.

Thus, the total fraction of the transformed phase should be proportional to the integral $\int_0^{t^{total}} \frac{d\varepsilon}{dt} dt = \varepsilon^{total}$, which correlates with our experimental findings.

Thus, steady state analysis gives the decomposition magnitude proportional to deformation time and deformation rate, which immediately gives the linear dependence on total deformation magnitude.

3. CREEP-INDUCED PHASE SEPARATION IN MULTIPHASE ALLOY

It is well known that actions of external field (electric current, thermal gradient) on solid solutions and on two-phase mixtures (solders) are drastically different. In solid solution, such action typically leads to very weak redistribution of components, because the drift generated by external field is very effectively opposed by the arising gradient of

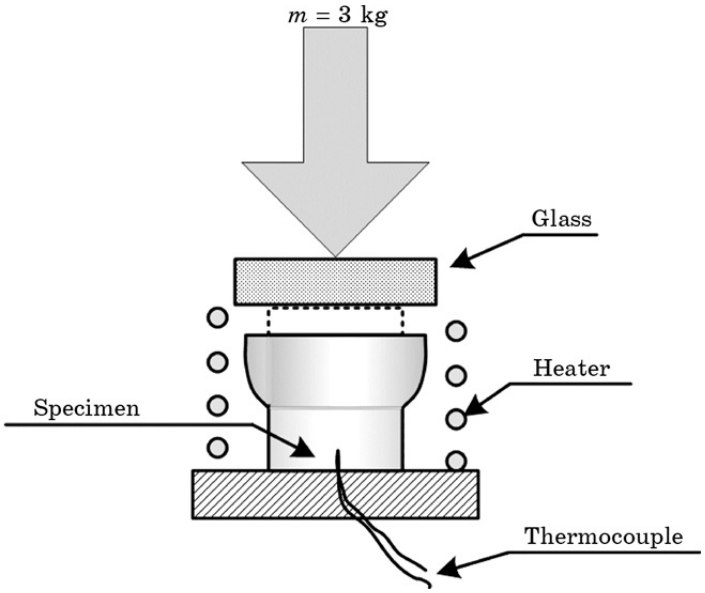

Fig. 5. Simplified scheme of the experimental set-up. Dot-line—sample boundary prior to deformation.

chemical potential (determined by concentration gradient).

In two-phase mixtures, the gradient of coarse-grained concentration is not anymore the driving force of diffusion; it means just the gradient of molar fractions of the phases, which remain in equilibrium with each other. Therefore, if the Gibbs–Thomson effect may be neglected, the redistribution of components due to external force is not opposed by equilibrant diffusion, so that this force can eventually lead to full spatial separation of phases. If one neglects the solubility of lead in tin and of tin in lead, the velocity of spatial separation of two-phase mixture can be roughly evaluated as $(D_1^* F_1 - D_2^* F_2)/(kT)$ where D_i^*, F_i are i-th components the diffusivity and the external force acting on the atoms of this component.

This is well known for electromigration in solders [8, 9] that high current density of about 100 millions of amperes per square meter passing through solder bump leads to full separation of tin and lead. The same happens under temperature gradient.

It seems natural to assume that the gradient of mechanical stress ($F_i = \Omega_I \, \mathrm{grad}\sigma$ with Ω_i being an atomic volume for i-th phase and σ is one-third of Spur of stress tensor) can also be an external force leading to separation of phases in the macroscopically homogeneous two-phase alloys. This hypothesis was checked at the solder Pb–Sn with eutectic composition. Superplastic alloys of such type, under constant loading and high temperature, demonstrate creep [10].

Cylindrical sample (diameter 10 mm and height 12 mm) was subjected to long-term loading in the special device (simplified scheme of experimental setup is shown in Fig. 5). Temperature was kept constant (20°C). Load was constant determining the constant deformation rate 15 mm/hour. Deformation was measured during experiment and reached 20%. Phase redistribution at the top of the sample was determined by electron probe microanalysis (EPMA). Composition of the central part is given in Table 2.

Character of deformation at the top and at the bottom appeared to be quite different. Upper part transformed into 'mushroom' of the height 10 mm and hat of diameter 14 mm. New-formed annular region had optical contrast typical for tin (see Fig. 6).

Radial concentration profiles measured by EPMA are shown at Fig. 7. One can see very distinct change of phase content ratio: annular region contains much more tin-based phase than the sample in average.

TABLE 2.

Composition of sample in the its central part (from EPMA)				
Element	O	Si	Sn	Pb
Weight, %	6.38	0.54	42.37	50.72

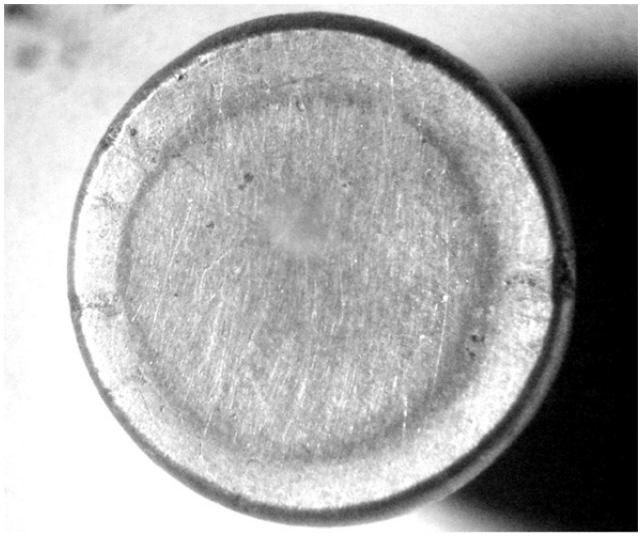

Fig. 6. Top view of the sample after 170 hours of creep.

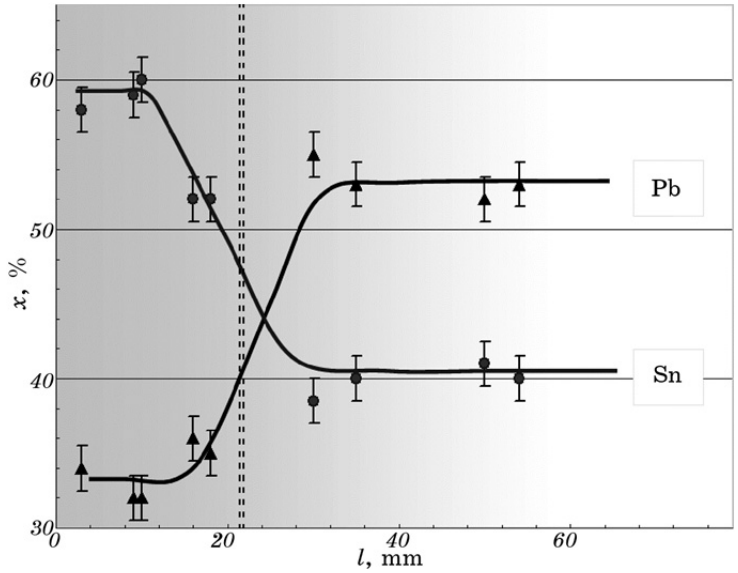

Fig. 7. Radial distribution of components after 170 hours of creep under load of 3 kg at temperature 160°C. Double dot-line indicates the position of margin before deformation.

4. CONCLUSIONS

Plastic deformation of tin–lead quenched alloy accelerates the decom-

position of tin solution in lead. Extent of decomposition is proportional to the total resulting deformation within broad interval of deformation rates.

Creep of the tin–lead two-phase alloy leads to spatial phase separation.

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