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Abstract

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Some Features of the Nucleation of Gray-Tin Centers on Particles of CdTe, InSb, Si, and Ge

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In work (^{1}) we showed that at temperatures below 0° an apparently reverse temperature course is observed for the coefficient of surface diffusion of mercury in tin. We associated this fact with the influence, on the course of the surface diffusion of mercury in tin, of the transformation β-Sn $\rightarrow$ α-Sn, which, as is known, always begins at the surface of the specimen. Work (^{1}) was carried out with tin specimens having a distorted surface, since in this case the effect of an increase in the diffusion rate of mercury at low temperatures appears especially clearly. When undistorted tin specimens are used, the rate of diffusion of mercury at low temperatures is so small that its measurement becomes difficult.

From previous work it is known that the transformation of white tin into gray tin can be accelerated both by the use of deformed specimens, as was done in (^{1}), and by the introduction of a seed. Until 1950 it was known that only crystallites of gray tin itself could serve as such a seed. In 1950 N. A. Goryunova (^{2}) showed that the transformation of white tin into gray tin can also be induced by crystallites of CdTe and InSb, which are isomorphous with α-Sn. These semiconductor compounds, like α-Sn, have a diamond-type lattice with parameters close to the lattice parameter of α-Sn. Since the question of the nucleation of centers of a new phase on various inclusions during phase transformations in solids is very important, it was of definite interest to check the influence of the above-mentioned substances on the initial stage of the transformation $\beta \rightarrow \alpha$-Sn, which can be judged by means of the method of surface diffusion of mercury (^{1}).

In work (^{2}) tin specimens were infected by rubbing in one or two crystallites of the substances being tested. Such a method of infection was unacceptable in our case, since for a substantial increase in the rate of diffusion of mercury in tin at low temperatures it is necessary for a large number of α-Sn centers to arise. The introduction of a large number of particles of CdTe, InSb, and also Si and Ge into the surface layer of white-tin specimens (chemically pure grade) was carried out as follows. A thin layer of rosin from its solution in acetone was applied to the inner surface of glass tubes. Then a certain amount of powder of one of the above-mentioned substances was placed in the tube, and by repeatedly shaking the tube it was uniformly coated from the inside with the powder; the excess of the latter was removed. In separate experiments (for example with Si) the tube was coated from the inside with particles from a suspension of the corresponding substance in a solution of rosin in acetone. The tubes prepared in this way were filled with molten tin, which after solidification was removed, and from the surface of the tin cylinders all particles that had not entered the surface layer were washed off with acetone. The procedure for studying the surface diffusion of mercury on these specimens differed little from that described in (1). The height of rise of the amalgam film was measured as a function of the holding time at various

temperatures. In work (3) it was shown that at room and higher temperatures this dependence has the form

$$h^2 \sim Dt \tag{1}$$

where h is the height of rise of the amalgam, t is the time of rise of the amalgam, and D is the coefficient of surface diffusion of mercury. At low temperatures, on distorted specimens this dependence becomes more complicated, and the curve $h^2(t)$ has an S-shaped character for $t > -24°$. As was shown in (1), the slowing of the rate of rise of the amalgam at large values of t is associated with relaxation of the stresses arising in the surface layer of white tin during the formation of α-Sn centers in the process of reactive surface diffusion of mercury.

Measurement of the rate of surface diffusion of mercury over tin with particles of CdTe, InSb, Si, and Ge introduced into its surface layer showed in all cases a sharp increase in it at low temperatures in comparison with undistorted tin (the least accelerating action was produced by Ge powder*). The influence of the amount of powders introduced into the surface layer of tin was also noted. Thus, in the case where a larger amount of CdTe had been deposited on one side of the tube, from this side of the specimen the amalgam rose faster than from the others. Thus, in the present case it is necessary to conclude that α-Sn centers nucleate on particles of insoluble impurities introduced into the surface layer of tin. Figure 1 gives plots of the dependence $h^2(t)$ at various low temperatures for one of the specimens Sn + CdTe**. On each of the plots the measurement temperature and the tangent of the angle of inclination of the straight line are indicated. From Fig. 1 it is seen that, for the holding times used, the dependence $h^2(t)$ is linear in all cases (except for the curve at $-8.8°$), without slowing at longer times. The curves $h^2(t)$ have the same character in all the other cases as well. The absence of slowing for long times is apparently due to the fact that, in the cases considered, the surface layer of the specimens is less loosened and that the "stability" of the α-Sn centers that arise is greater when they nucleate on particles of impurities insoluble in β-Sn, especially if these impurities are isomorphous with α-Sn. Also deserving attention is the fact that, according to our measurements (Fig. 1), when the temperature is lowered the measured coefficient of surface diffusion of mercury increases (as earlier in work (1)), and then at temperatures of $-18°$ and below in some cases decreases,

Fig. 1. Dependence $h^2(t)$ at low temperatures for Sn + CdTe specimens (see curve 11 in Fig. 2)

Figure 1: Fig. 1. Dependence $h^2(t)$ at low temperatures for Sn + CdTe specimens (see curve 11 in Fig. 2)

Fig. 2. Temperature dependence of the coefficient of surface diffusion of mercury in tin amalgam on samples Sn + CdTe (I, II), Sn + Ge (III), Sn + Si (IV, V), and Sn + InSb (VI)

Figure 2: Fig. 2. Temperature dependence of the coefficient of surface diffusion of mercury in tin amalgam on samples Sn + CdTe (I, II), Sn + Ge (III), Sn + Si (IV, V), and Sn + InSb (VI)

which had not been observed previously. In the present work a similar effect was repeatedly observed on tin specimens with CdTe and Si powders introduced into their surface layer. In experiments with specimens Sn + InSb and Sn + Ge, we did not observe such a low-temperature maximum of the coefficient of surface diffusion of mercury. Figure 2 gives plots of the dependence of $\operatorname{tg}\alpha$ (a quantity proportional to the coefficient of surface diffusion) on

Fig. 1. Dependence $h^2(t)$ at low temperatures for Sn + CdTe specimens (see curve 11 in Fig. 2)

Curves	T, °C	$\operatorname{tg}\alpha$	Curves	T, °C	$\operatorname{tg}\alpha$
a	−8.8	$\operatorname{tg}_1 = 0.31$; $\operatorname{tg}_2 = 0.16$	g	−18.7	0.85
b	−12.2	0.41	d	−22	1.29
v	−15.4	0.51	e	−27.2	0.85
			zh	−28.6	0.78

* We did not observe such an accelerating action when graphite powder was introduced into the glass tube.
** Some curves are displaced along the ordinate axis.

temperatures for the samples Sn + CdTe, Sn + Ge, Sn + Si, and Sn + InSb. In the case of Sn + CdTe and Sn + Si this was observed at several temperature points on the descending branch of the curve $\operatorname{tg}\alpha(T)$, which convincingly indicates the presence in these cases of a low-temperature maximum. It appears to us that the reason for the existence of such a maximum is as follows.

Already in work (^{1}) it was noted that the number of sites for the formation of α-Sn nuclei at a given low temperature is limited, and that the total number of nuclei arising at these "prepared sites" increases as the temperature is lowered.

Fig. 2. Temperature dependence of the coefficient of surface diffusion of mercury in tin amalgam on samples Sn + CdTe (*I, II*), Sn + Ge (*III*), Sn + Si (*IV, V*), and Sn + InSb (*VI*).

Such an increase is connected with the fact that, with increasing supercooling, the critical size of a nucleus of the new phase decreases both in spontaneous formation of nuclei and in their nucleation on particles of insoluble impurities and other structural imperfections. Such an increase in the number of centers of the new phase with increasing supercooling is understandable, since in any object under study there is apparently some distribution of the corresponding regions according to size and "activity." It may be assumed, however, that in the case when a certain uniformity of the "prepared sites" has been created, at some supercooling the overwhelming majority of them will be exhausted, and then a further lowering of the temperature will no longer substantially increase the number of nuclei of gray tin; consequently, in the system now already relatively stable (β-Sn + a definite number of α-Sn centers), the coefficient of surface diffusion of mercury upon further cooling will decrease, as is in fact observed experimentally. Naturally, when particles of insoluble impurities are introduced into the surface layer of tin, there is a greater uniformity of the "prepared sites" than in the case of the inhomogeneously stressed state that was produced by deformation of the initial samples in work ([1]).

In works ([2],[4]) it was noted that only CdTe and InSb crystallites, and not many other substances, including Ge and Si, exert a seeding effect on the $\beta \rightarrow \alpha$-Sn transformation. In this connection it must be noted that in our experiments the influence of the introduced insoluble impurities on the initial stages of the transformation of white tin into gray was recorded, whereas in works ([2],[4]) its later stages were investigated. Therefore the influence of the particles indicated above, which we detected, is not a condition sufficient for the manifestation of their accelerating action in such experiments as those of N. A. Goryunova ([2],[4]). It is also possible that sintering of insoluble

the introduction of particles into tin has a more effective influence on the nucleation of centers of gray tin than does rubbing them in.

In conclusion, I take this opportunity to express my gratitude to Prof. S. D. Gertsriken for supervising the work.

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Note: Figure translations are in progress. See original paper for figures.