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The transition temperature of the transition between grey and white tin

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Systematic experiments, using a sensitive dilatometric technique, have been carried out on the transformation temperatures of two samples of metallic tin and of a number of dilute tin-rich alloys. Vulcan tin (99·997 % pure—major impurity iron) transforms in the temperature range 9·9 to 10·8° C, while Pass-S tin (also 99·997 % pure—major impurity lead) transforms in the range 13·0 to 13·6° C. The transformation temperature observed for a given sample is higher the greater its 'activity' (as measured by the time necessary to secure 40 % transformation from grey tin to white tin at 30° C), suggesting that the observed change point is a function of the strain energy of the white tin formed.

Additions of lead, bismuth, antimony and tellurium in the range 0·001 to 0·005 at. % raise the apparent transformation temperature of Vulcan tin, while similar quantities of zinc and aluminium have little effect. Substantial additions of zinc, aluminium, tellurium and germanium lower the observed transformation temperature of Vulcan tin. The results are discussed and it is suggested that those elements which raise the transformation temperature do so by increasing the degree to which strain energy may be retained in the white tin formed by the transformation.

1. INTRODUCTION

The transformation of white tin to grey tin at temperatures in the region of 0° C is frequently quoted as a classical example of allotropy. The determination of the transition temperature, however, is difficult and doubt exists about the precise value. Thus, experiments using an electrolytic cell, the composition of which may be represented as 'white tin/10 % ammonium stannic chloride solution/grey tin', gave a value of approximately 20° C and later, of 18° C (Cohen & van Eijk 1899, 1900). A third determination, using dilatometric methods (Cohen & Decker 1927), gave a transition temperature of 12 to 14·3° C; the most recent value, obtained by using a highly active material prepared by thermal cycling, is reported as 13·2 ± 0·1° C (Cohen & van Lieshout 1935). Experiments in the authors' laboratory on certain general features of the transformation suggested that the transformation temperature should be reinvestigated to serve as a basis of comparison for work on the effect of small alloying additions on the transformation. The present paper reports work on two different grades of 'pure' tin, and certain very dilute alloys, using a dilatometric method.

2. MATERIALS AND EXPERIMENTAL METHODS

Two specimens of tin were investigated; the compositions are given in table 1. Specimens were used in the 'as-received' (cast) condition; a few grains of grey tin were added to the charged dilatometers, which were fitted with capillary necks, before filling with xylene as the dilatometric fluid. Storage at the temperature of solid carbon dioxide for 3 to 4 days resulted in complete transformation to grey tin;

specimens were then held for 40 min at 45° C to obtain transformation back to white tin, and returned to the 'dry ice' enclosure for transformation to the grey variety. By repetition of this process at least ten times very finely divided and active material was obtained. A maximum $\alpha \rightarrow \beta$* velocity at a given temperature is generally observed when approximately 40 % transformation has taken place. Specimens were thus approximately 40 % transformed into white tin, before the dilatometer was transferred to the transformation thermostat for rate determination. All specimens were therefore observed after establishing a comparable initial condition. The thermostat enclosure used for the determination of transition points operated from 15 to −40° C; cooling was achieved by means of a modified commercial refrigerator, and specimens were immersed almost to the level of the meniscus of the dilatometer in a well-stirred ethyl alcohol + water mixture, the temperature of which could be kept constant to within $\frac{1}{250}$° C over periods up to 8 h and to within $\frac{1}{100}$° C over longer periods. The height of the meniscus was observed through a window of low thermal conductivity by means of a cathetometer, the telescope carriage of which was fitted with a vernier, allowing readings to be made to 0·01 mm over a distance of 50 cm.

TABLE 1

specimen	Pb	Sb	Fe	As	Cu	Bi	S	Sn by difference*
Vulcan tin	0·0005	0·0002	0·0020	0·0001	—	—	—	99·9972
Pass-S tin	0·0012	0·0010	0·0002	0·0002	0·0002	0·0001	trace?	99·9970

* No elements other than those noted were detected.

After any change in the temperature of the transformation thermostat, in which several dilatometers could be accommodated simultaneously, at least 1 h was allowed to elapse for the establishment of thermal equilibrium. The telescope was then focused on the meniscus of a control dilatometer containing no tin, and the corresponding reading noted. Similar settings were then made on each of the experimental dilatometers in the enclosure in a fixed order; this procedure was repeated, and a final setting made upon the control dilatometer. In this way a check was kept on the accuracy of temperature control during the observation period, since the control dilatometer acted as a sensitive thermometer, a change in bath temperature of $\frac{1}{100}$° C corresponding to a change in meniscus height of 2 mm.

The observation sequence was repeated at appropriate time intervals and accurate rate of transformation measurements were obtained. Temperatures were measured with N.P.L. standardized thermometers graduated in $\frac{1}{50}$° C enabling readings to be made to $\frac{1}{200}$° C.

3. RESULTS

(a) *Vulcan tin*

Eleven specimens were examined. Typical results, obtained from two series of tests with four specimens, appear in table 2. The times required for the 40 % transformation prior to examination are given as an indication of the activity of each

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* In this paper, α refers to grey tin, and β to white tin.

specimen, together with the chronological order in which individual tests were carried out. Transformation temperatures were observed between 9·9 and 10·8° C.

(*b*) *Pass-S tin*

Seven specimens were used, and table 3 summarizes typical results from two series of tests on three of these. In this case, transformation temperatures were observed to lie between 13 and 13·6° C. This is a very significant difference from the results for Vulcan tin, which is nominally of the same overall purity, differing only in the nature of the impurities.

TABLE 2. VULCAN TIN

temp. (° C)	duration of test (h)	order	rate of change of dilatometer level (cm/h)			
			*RV*1	*RV*2	*S*1	*S*9
9·53	20	9	+0·05	+0·04	+0·12	+0·02
9·78	40	8	+0·09	+0·03	+0·22	+0·06
9·98	20	10	+0·04	+0·01	0·00	−0·02
10·06	40	7	+0·07	+0·06	+0·18	+0·06
10·32	24	1	+0·11	+0·05	+0·50	+0·13
10·42	50	6	0·00	−0·15	+0·03	−0·07
10·52	25	2	+0·02	−0·02	+0·17	+0·04
10·70	70	3	0·00	−0·10	+0·24	+0·06
10·90	65	5	−0·06	−0·30	−0·09	−0·08
11·10	60	4	−0·23	−0·42	−0·20	−0·01
time for 40 % $\alpha \rightarrow \beta$ *at* 30° C (*min*)			180	180	90	180
9·94	23	1	+0·15	+0·10	+0·20	0·00
9·98	20	5	−0·01	−0·03	+0·04	—
10·05	16	4	−0·02	−0·03	+0·01	—
10·16	20	3	−0·04	−0·01	+0·04	−0·02
10·32	12	2	−0·05	−0·05	−0·01	−0·06
time for 40 % $\alpha \rightarrow \beta$ *at* 30° C (*min*)			>250	>250	150	>250

Notes. (1) Specimens *RV*1, *RV*2, *S*1 and *S*9 were respectively 60, 60, 77·5 and 70·0 g Vulcan tin in xylene.

(2) For specimens *RV*1, *RV*2 and *S*9 in the second series of tests, 40 % conversion to β was not complete after 250 min at 30° C, but could be completed by an additional 1 min at 45° C.

(3) Positive rates correspond to $\beta \rightarrow \alpha$; negative rates correspond to $\alpha \rightarrow \beta$.

(*c*) *Nature of results*

A detailed analysis of the results showed that, if the sequence of tests was such that observations at closely similar temperatures were made near the beginning and near the end of the sequence, there was a general tendency (i) for rates of change which were positive early in the test sequence to decrease, or to become zero or slightly negative in the later observation, and (ii) for rates of change which were negative early in the sequence to remain negative but to increase numerically in the later observation. These tendencies are illustrated by observations 1 and 6 in the upper portion of table 2, by observations 1 and 5 in the lower portion of table 2, and by observations 1 and 9 in the upper portion of table 3. This behaviour is consistent with a gradual lowering of the transformation temperature as the sequence of tests proceeds.

(*d*) *Dilute alloys*

For comparison with the tin samples, dilute alloys containing 0·001 to 0·005 at. % of bismuth, antimony, lead, aluminium, zinc, iron and tellurium were prepared in quantities of 60 g by melting tin with carefully analyzed master alloys *in vacuo*, and quenching the resulting melt. The ingots were homogenized for 50 h at 200° C, and air cooled; a 50 g sample of each specimen of pure tin was treated similarly to provide suitable controls.

TABLE 3. PASS-S TIN

temp. (° C)	duration of test (h)	order	rate of change of dilatometer level (cm/h)		
			RS 2	*C*	*SA*
12·98	16	8	+0·18	+0·03	+0·20
13·22	15	1	+0·34	−0·04	+0·05
13·24	16	9	+0·03	−0·25	−0·01
13·42	14	4	+0·01	+0·12	+0·08
13·54	17	2	−0·02	−0·20	+0·03
13·54	14	5	+0·04	−0·06	+0·02
13·60	22	7	0·00	−0·05	−0·01
13·66	15	6	−0·02	−0·06	−0·03
13·98	18	3	−0·42	−0·20	−0·25
time for 40 % $\alpha \rightarrow \beta$ *at* 30° C (*min*)			40	>200	60
12·99	20	7	+0·02	+0·02	+0·01
13·03	36	6	−0·04	+0·10	+0·02
13·08	40	5	−0·06	+0·01	+0·01
13·12	44	1	+0·09	+0·19	+0·40
13·20	40	2	−0·05	0·00	−0·10
13·27	24	4	−0·07	+0·08	−0·02
13·36	30	3	−0·54	−0·07	−2·29
time for 40 % $\alpha \rightarrow \beta$ *at* 30° C (*min*)			55	>300	65

Notes. (1) Specimens *RS* 2 and *SA* were respectively 60 and 120 g Pass-S tin in xylene; specimen *C* was 180 g tin in a solution of 'pink-salt' ($(NH_4)_2SnCl_6$) in ethyl alcohol, saturated at −50° C.

(2) Specimen *C* in the first series of tests required 200 min at 30° C and an additional 20 min at 45° C to secure 40 % conversion to β; in the second series this specimen required 300 min at 30° C plus 15 min at 45° C.

All specimens were examined as described for pure tin, except for the alloy containing 0·005 at. % of lead which was only partially transformed after 2 months at the temperature of solid carbon dioxide. The results of the transformation tests are collected in table 4*. A few more concentrated alloys containing 0·05 at. % aluminium, 4 at. % zinc, 2 at. % tellurium and 0·06 at. % germanium were also prepared. These required 4 months at the solid carbon dioxide temperature before transformation to α was complete in all cases. The first three specimens were thermally cycled as for the dilute alloys, but that containing germanium failed to revert to β after 30 min at 43° C, in agreement with the work of Ewald (1954),

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* For ease of reference, individual alloys are designated by the prefix *V* if made from Vulcan tin, or *S* if made from Pass-S tin, by a numeral denoting the atomic percentage of solute $\times 10^3$, and the chemical symbol of the solute. Thus the alloy containing 0·005 at. % of lead is denoted *V* 5 Pb.

TABLE 4

temp. (° C)	duration of test (h)	order in ser. 1	order in ser. 2	rate of change of dilatometer level (cm/h)													
				Vulcan	Pass-S	*V* 1 Pb	*V* 1 Bi	*V* 2 Bi	*V* 5 Bi	*V* 1 Sb	*V* 2 Sb	*V* 5 Sb	*V* 5 Al	*V* 5 Te	*V* 5 Zn	*S* 5 Zn	*S* 5 Fe
10·00	12	1	—	+0·83	—	—	+0·58	—	—	+0·18	—	—	+0·55	+5·60	+1·32	—	—
10·52	18	2	—	+0·33	—	—	+0·30	—	—	+0·56	—	+1·63	+0·20	—	+0·60	—	—
11·12	13	3	—	+0·07	—	—	+0·01	—	—	+0·08	—	+0·28	+0·04	—	+0·08	—	—
11·54	20	4	—	+0·03	—	—	+0·01	—	—	+0·05	—	+0·26	+0·01	—	+0·05	—	—
11·64	15	6	—	+0·04	—	—	+0·02	—	—	+0·10	+0·03	—	+0·03	—	+0·05	—	—
11·75	19	7	—	+0·01	—	—	+0·01	—	—	+0·04	0·00	—	0·00	—	+0·03	—	—
11·89	13	5	—	−0·09	—	—	−0·22	—	—	−0·08	−0·10	—	−0·07	—	−0·10	—	—
11·94	38	—	9	−0·02	+1·10	—	0·00	—	—	−0·01	−0·10	—	−0·03	—	−0·01	—	—
12·13	20	8	—	−0·05	—	—	−0·04	—	—	−0·02	−0·06	—	−0·03	—	−0·01	—	—
12·53	27	—	4	—	+0·41	+0·57	—	+0·56	+0·45	—	−0·02	—	—	+0·45	—	+0·40	+0·64
12·72	20	—	10	−0·08	0·00	—	−0·09	—	—	−0·09	−0·05	—	−0·07	—	−0·07	—	—
12·78	14	—	8	—	+0·02	+0·19	—	+0·21	+0·10	—	—	+0·06	—	+0·14	—	+0·08	+0·11
13·02	13	—	3	—	+0·11	+0·26	—	+0·25	+0·17	—	−0·02	—	—	+0·08	—	+0·13	+0·27
13·29	14	—	5	—	+0·10	+0·09	—	+0·19	+0·11	—	−0·08	−0·08	—	+0·05	—	+0·13	+0·05
13·58	21	—	7	—	−0·03	+0·02	—	−0·03	−0·03	—	—	−0·10	—	−0·08	—	−0·02	−0·01
13·59	11	—	1	—	−0·03	+0·02	—	+1·13	+0·04	—	0·00	−0·10	—	—	—	−0·09	−0·06
13·73	17	—	6	—	−0·10	−0·09	—	−0·12	−0·10	—	—	−0·25	—	−0·22	—	−0·12	−0·10
13·92	20	—	2	—	−0·04	−0·09	—	−0·14	−0·16	—	−0·03	—	—	−0·68	—	−0·25	−0·21
time for 40 % $\alpha \rightarrow \beta$ *at* 30° C (*min*)				60	50	35	45	35	25	50	95	25	35	70	50	20	20

who, while studying the semiconducting properties of grey tin, found that transformation to β occurred at appreciable rates only above 60° C. In the thermal cycling to produce an active specimen, therefore, the $\alpha \rightarrow \beta$ change was carried out at 70° C for about 7 min. After twenty-two transformations the specimen was examined dilatometrically, and showed a very small volume decrease, corresponding to the formation of white tin, at all temperatures down to 7° C, the lowest reached in the tests. The dilatometric results for the other more concentrated alloys are given in table 5.

TABLE 5

temp. (° C)	duration of test (h)	order	rate of change of dilatometer level (cm/h)		
			V 50 Al	*V* 4000 Zn	*V* 2000 Te
7·15	40	3	+0·40	+0·21	−0·212
8·5	36	4	−0·03	−0·03	−0·12
10·20	18	2	−0·21	−0·35	−0·251
15·80	40	1	−1·26	−1·74	−0·54
time for 40 % $\alpha \rightarrow \beta$ *at* 30° C (*min*)			> 60*	25	> 60†

* This specimen transformed 40 % by 60 min at 30° C plus 30 min at 35° C.
† This specimen transformed 40 % by 60 min at 30° C plus 30 min at 43° C.

4. DISCUSSION

(*a*) *Tin specimens*

Tables 2 and 3 show that Vulcan and Pass-S tin transform within temperature ranges which are significantly different. Further, separate specimens of the same type of tin transform at slightly different temperatures. There is, however, a clear correlation between the temperature at which the sign of the dilation changes from positive to negative and the activity of the specimen (i.e. the time required for 40 % transformation). Thus, when specimen *S* 1 required 90 min for 40 % conversion, sign reversal occurred at 10·8° C. The reversal occurred, however, in the region of 10·3° C for specimens *RV* 1, *RV* 2 and *S* 9 (180 min for 40 % conversion), and also for *S* 1 itself when it was in such a condition as to require 150 min for 40 % conversion. Similarly, a decrease of the temperature of sign reversal occurs for *RV* 1, *RV* 2 and *S* 9 as the time required for 40 % conversion to β increases. Inspection of table 3 shows similar tendencies, in that, as the time for the preliminary 40 % $\alpha \rightarrow \beta$ transformation increases, the temperature of sign reversal decreases from approximately 13·6 to 13·0° C. It is also of interest that positive transformation rates at temperatures outside the range in which sign reversal occurs in general decreased as a series of tests progresses; this is illustrated for *RS* 2 by tests 1 and 9 in the upper portion of table 3, where the rate of change of dilatometer level fell from +0·34 to +0·03 cm/h over a period of about 10 days, in spite of the very similar test temperatures.

The observed transition temperature is thus dependent upon the precise condition of the material. Highly active α material produced by thermal cycling consists of very fine grey tin particles and corresponds with a very high specific surface on which the white modification may be nucleated, giving rise to the high transformation rate. Under such conditions the white tin produced, especially if it forms a shell coherent with the underlying grey tin as suggested by Dunkerley & Munge (1950), will be highly strained. White tin formed more slowly in less active specimens on the surface of larger particles of grey tin is less likely to be subjected to such high transformation strains. It is probable that the corresponding strain energy, which will vary according to the rate at which white tin is formed and according to the length of time available for recrystallization or relief of strain, is responsible for the systematically variable results obtained. In figure 1 hypothetical free-energy curves are drawn for the transformation in strain-free material, intersecting at the true transformation temperature T_c. If, however, the white tin formed is highly strained, the corresponding free-energy curve will be raised (curve S); since brittle grey tin cannot support lattice strains to the same extent as the white modification, the corresponding free-energy curve will be little affected, and the change is neglected, for simplicity, in figure 1. The strain-energy contribution in white tin may be expected to decrease slowly with time, so that at any given moment of observation the appropriate free-energy curve may be represented by curve O. The intersection now occurs at the higher temperature T_0; the interval T_0—T_c will depend upon the precise condition of the thermally cycled material with which the test was made, and the stage of the test corresponding with the individual observations. The lower observed transition points obtained with the less active samples are thus likely to be nearer the true transition temperature T_c. Relaxation of the stresses in white tin during the progress of a test will tend to lower the observed transition temperature, and evidence for this appears in tables 2 and 3, as already described.

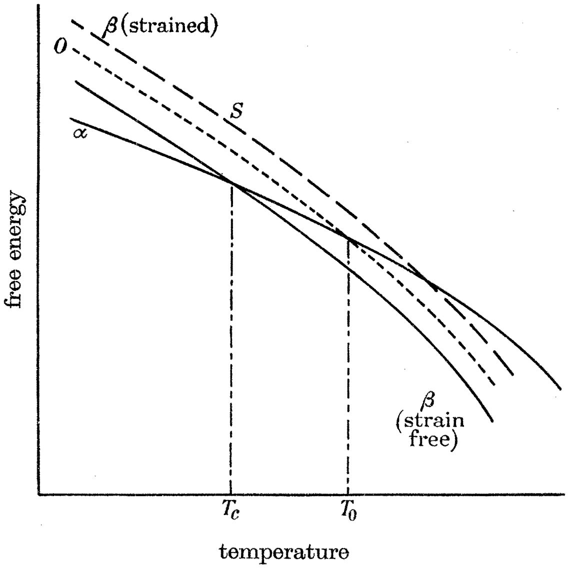

FIGURE 1. Hypothetical free-energy curves for the white tin ⇌ grey tin transformation.

(b) *Tin-rich alloys*

Inspection of table 4 shows that annealed Pass-S material has substantially the same observed transition point as the cast material, while the transition temperature for Vulcan tin is raised by annealing. This may be understood since the principal impurity in Pass-S tin is lead, which is likely to be in solid solution in both the cast and annealed states, while the chief impurity in Vulcan tin is iron, which is expected to separate from supersaturated solid solution on annealing. Taking the Vulcan specimen as standard, the observed transformation temperature is raised, in decreasing order of effectiveness, by lead, bismuth and antimony, 0·001 at. % lead being more effective than 0·005 at. % of the other elements. Of particular interest is the effect of 0·001 at. % lead, which changes the characteristics of Vulcan tin to those of Pass-S, in conformity with the reported impurity contents of these materials. The solutes which raise the transformation temperature have been reported in the literature to retard the $\beta \rightarrow \alpha$ change, and are soluble, in the amounts used, in white tin.

Zinc and aluminium, both of which accelerate the $\beta \rightarrow \alpha$ change, affect the transformation temperature only slightly, but 0·005 at. % tellurium moves this temperature into the range characteristic of Pass-S tin. Additions of 0·005 at. % of zinc and iron to Pass-S tin would appear to reduce the transformation temperature slightly when allowance is made for the highly active state of these specimens in table 4.

Table 5 suggests that higher concentrations of ‘accelerators’, including tellurium, reduce the transformation temperature appreciably.

The increase in the transformation temperature caused by lead, bismuth, tellurium and antimony implies either that the free energy/temperature curve of grey tin is lowered, or that the corresponding curve for white tin is raised. The former possibility would imply a greater solubility of the solutes in grey tin than in white, which is unlikely. The solid solution of these elements in white tin, however, corresponds to a relative lowering of the free energy/temperature curve for white tin, leading to the depression of the transformation temperature, as observed for substantial additions of aluminium, zinc, tellurium and germanium. It is suggested, therefore, that the role of solutes which raise the transformation temperature in dilute alloys is to increase (e.g. by interaction with dislocations) the degree to which the internal strains in the white tin formed may be retained. The small decrease in free energy due to alloying very small quantities of solute elements will be offset by the strain energy, giving a free energy/temperature curve such as curve S in figure 1. As compared with unalloyed tin, the rate of stress relaxation in the presence of the solute elements will be decreased, so that in tests of similar type and duration to those carried out on unalloyed tin, an observed transition point intermediate between T_0 and T_c in figure 1 is obtained.

It must be assumed that zinc and aluminium, which in small quantities do not affect the transition temperature, but decrease it when present in larger amounts, are less effective in preventing the relaxation of the internal stresses in white tin.

The dilatometrically observed transition temperature of the grey tin → white tin transformation is thus dependent upon the condition of the material, and does not correspond to the true change point, while the effect of small additions of other elements depends upon their efficiency in retaining the white tin formed in a state of high internal strain. Another method for attempting to obtain a close approximation to the transformation temperature would be that involving the electromotive force of an electrolytic cell having electrodes of grey and white tin, but, in the authors' experience, the reproducibility of the results is insufficient for critical work.

The work described forms part of a wider programme on the transformation of tin, which has been in progress in the University of Birmingham. Grateful acknowledgement is made to the Tin Research Institute for sponsoring one of us (R. W. S.) and for financial assistance which, together with that from Imperial Chemical Industries Ltd, has greatly assisted the work.

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