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EFFECT OF GERMANIUM ON THE TRANSFORMATION OF WHITE TO GRAY TIN, AT COMPARATIVELY LOW TEMPERATURE[1]

by

R. R. Rogers and J. F. Fydell

ABSTRACT

At a comparatively low temperature, gray tin may appear on white tin when the latter (a) is in contact with elementary germanium, (b) contains a certain proportion of germanium in the form of an alloy, or (c) is in contact with solutions in which certain germanium compounds have been dissolved. Data also are presented regarding the rate of spread of gray tin on white tin castings and coatings containing various proportions of germanium.

INTRODUCTION

Ordinary tin, which is ductile and useful for many important purposes, is stable above 13.2°C (55.8°F). On the other hand, gray tin, which is quite brittle and useless for most purposes, is stable below that temperature. Fortunately the transformation to gray tin frequently occurs very slowly, although at times it does take place with considerable rapidity. Even after the gray tin has been reconverted into the white variety by increase in temperature the material usually is of little value until it has been remelted.

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The term "tin disease" has been used in the literature when referring to this phenomenon, probably due to the wart-like appearance of the gray tin, and to the fact that a sample of gray tin may "inoculate" samples of white tin which are in contact with it. Sometimes the first indication of the transformation appears spontaneously, i.e., without inoculation.

A summary of the previously published information on gray tin has been compiled (1). From this it would appear that much remains to be learned regarding the subject. For this reason a research program was initiated at the Mines Branch of the Department of Mines and Technical Surveys to investigate the various factors which have an influence on the transformation to gray tin. During this research it became evident that germanium, when present, may have a considerable effect on the transformation. The results of the experiments which were performed in this connection are given in the present paper. It is expected that data obtained during work on other phases of the gray tin problem may be published later.

Although the authors have not investigated this phase of the problem extensively, it is of interest to note that germanium has been found in certain tin minerals. Papish (2) reported the presence of this element in five of the twelve tin minerals which he investigated, the proportion varying between 0.001 and more than 0.005 per cent. The sources of these germanium-containing minerals were: Yukon, Nevada, Mexico, Bolivia, and New South Wales.

The tin used in all of the present experiments was obtained in the form of cast bars, and the following analysis was supplied by the manufacturer: antimony, 0.0005%; lead, 0.0005%; copper, 0.0002%; bismuth, 0.0002%; iron, 0.0002%; arsenic, trace; silver, trace.

The sulphur content was found to be 0.006 per cent in these laboratories. This tin will be referred to as "pure tin" in this paper.

The germanium used was a pure grade obtained from the Eagle-Picher Company of Cincinnati, Ohio.

EXPERIMENTAL

Cast Tin and Tin Alloys

It is known that different types of tin have different degrees of susceptibility to gray tin formation. Early in the investigation it was found that the pure tin used in these experiments had quite a high susceptibility. A cast bar 12.3 cm (5 in.) long x 0.8 cm (0.3 in.) in diameter (Fig. 1, page 4) was converted completely into gray tin (Fig. 2, page 4) in 13 days when inoculated with gray tin and exposed to a temperature of -30°C. The gray tin appeared approximately one day after inoculation.

Later experiments showed that similar results could be obtained if elementary germanium was used as the inoculating agent instead of gray tin. While in contact, the tin and germanium were immersed in an aqueous solution containing calcium chloride (450 g/l) acidified with hydrochloric acid to pH 1.5. The gray tin appeared approximately two days after inoculation.

Gray tin was produced on similar bars of pure tin when they were immersed for four months in calcium chloride solution

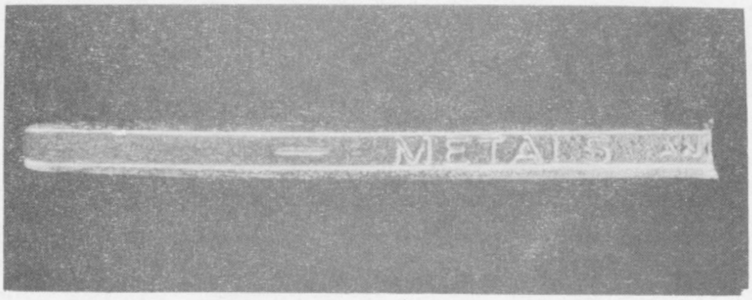

Fig. 1. A 5-in. cast bar of commercially pure tin prior to inoculation with gray tin.

Fig. 2. The cast bar of commercially pure tin shown in Fig. 1 after inoculation with gray tin and 13 days at -30°C.

(450 g/l) in which germanium dioxide (0.15 g/l) had been dissolved. The temperature was maintained at -30°C throughout the experiment. No such result was obtained in the absence of germanium dioxide.

In some of these experiments the germanium dioxide was replaced by a soluble salt of one of the following metals; bismuth, antimony, silver, copper (ic), lead, iron (ous), lithium, zinc. Although some of the more noble of these metals were deposited on the tin bars by electrolytic replacement, no evidence of gray tin formation was observed.

A number of small pure tin castings of the same size and shape, containing various proportions of germanium and zinc, were produced and then exposed to temperatures of +4°, -29°, -40°, and -51°C (40°, -20°, -40°, and -60°F) without inoculation. The length of time which elapsed before gray tin appeared spontaneously on each casting is given in Table I.

The rate of spread (m) of the gray tin on these castings is given in Table II. (Note: In this research it has been found that the relation $A^{1/2} = mt + b$ exists where A is the area in square millimeters which has been infected with gray tin in t days, and b is a constant for any particular area. Although the dilatometer method of measuring rate of spread has been used considerably in the past, it is not applicable in the case of comparatively thin coatings. In the present work the same method of measuring rate of spread was used for both coatings and castings, in order to permit comparisons to be made.)

TABLE I

Spontaneous formation of gray tin on castings.

Composition (wt. %)			Time to spontaneous appearance of gray tin (days)			
Sn	Ge	Zn	+4°C	-29°C	-40°C	-51°C
100	-	-	>220*	31	>56*	1.9
98	2	-	>220*	4	0.9	0.9
86	14	-	>220*	0.9	0.9	0.9
98	-	2	>220*	41	7	5.9
96	2	2	>220*	14	14	4.0

*

No gray tin had formed on samples within period stated and experiment was discontinued.

TABLE II

m values for gray tin on castings.

Composition (wt, %)			m		
Sn	Ge	Zn	-29°C	-40°C	-51°C
100	-	-	1.41	-	4.9
98	2	-	0.9	3.7	0.85
86	14	-	0.38	4.6	3.3
98	-	2	0.07	0.43	0.07
96	2	2	0.03	0.03	0.12

Hot Dip Tin Coatings

Sheet steel coupons were electroplated on both sides with about 0.005 cm (0.002 in.) of iron, following a procedure previously used (3). After rinsing in water and then in a slightly acidified aqueous solution of the flux, they were dipped into a molten bath of pure tin which was covered with molten flux ($ZnCl_2$ 75%, NaCl 11%, KCl 14%) and was operated at a temperature of 306±2°C (583°F). Various small amounts of germanium were added to the molten bath and a number of the plated steel coupons were dipped in the bath after each addition. The germanium content of the resulting coatings was determined spectrographically.

Coupons with tin coatings having different germanium contents were exposed to temperatures of -29°, -40°, and -51°C. Those in which spontaneous transformation to gray tin occurred, and the length of time required in each case, are given in Table III. In every case except one, this transformation took place in the comparatively thick coating at the bottom of the coupon.

A similar set of coupons was inoculated with gray tin and exposed to the same temperatures. The rate of spread of the gray tin on each coupon was determined. The values of m are given in Table IV.

TABLE III

Spontaneous formation of gray tin on coatings.

Germanium content (wt, %)	Time to spontaneous appearance (days)		
	-29°C	-40°C	-51°C
0.00	>370*	>37*	0.8
0.01	>370*	12	>4.9*
0.03	88	18	>4.9*
0.12	32	2.7	1.7
0.17	17	1.7	0.8
0.45	17	0.9	1.7
1.10	17	0.7	1.7

* No gray tin had formed on sample within period stated and experiment was discontinued.

TABLE IV

m values for gray tin on coatings.

Germanium content (wt, %)	m -20°C	-40°C	-51°C
0.00	0.06	0.32	0.70
0.01	0.07	0.11	0.87
0.03	0.07	0.11	0.34
0.12	0.08	0.05	0.86
0.17	0.04	0.11	3.00
0.45	0.04	0.34	2.30
1.10	0.03	0.11	0.05
Average	0.06	0.16	1.16

DISCUSSION

It was shown that white tin of the type used in these experiments could be transformed into gray tin when the former was brought into contact with a particle of gray tin at a suitable temperature. This phenomenon has been known for a considerable number of years.

It was also shown that the white tin could be transformed into gray tin when the former was brought into contact with a particle of elementary germanium in the presence of acidified calcium chloride solution at a suitable temperature. No transformation took place when the white tin was in contact with the acidified chloride solution only. A concentrated solution of calcium chloride was used because such a solution does not freeze at -30°C. No doubt a solution of any other electrolyte which would remain liquid at this temperature would give similar results. Apparently the function of the acid in the solution was to keep the surfaces of the germanium and tin free from oxides or other compounds. Films of such compounds would have prevented a direct contact between germanium and tin.

The transformation took place in the presence of an aqueous solution in which germanium dioxide had been dissolved. It is assumed that elementary germanium was slowly deposited on the white tin by electrolytic replacement and this caused the transformation to gray tin by inoculation. No doubt solutions containing a number of other germanium compounds would have given the same result.

It also was shown that the transformation to gray tin did not take place when solutions of a wide variety of metal salts were in contact with the white tin. This was true even when a metal such as silver or copper was deposited on the tin by electrolytic replacement.

At a suitable temperature, gray tin appeared spontaneously on tin castings containing certain proportions of germanium. It would appear from the constitutional diagram (4) that elementary germanium separates out when alloys of tin and germanium are cooled below 232°C. It is assumed that this particular germanium acted similarly to that used in producing gray tin by inoculation. The time which elapsed before the spontaneous appearance took place was decreased as the germanium content was increased. When zinc was present in the alloy the time which elapsed was increased. This may be caused by the fact that the gray tin was produced in a tin-zinc combination rather than in tin alone. Zinc was used in some of these experiments because it tends to increase the rate of spread of gray tin, when it is present in certain proportions.

It was shown that the rate of spread (m) of gray tin was greatest on the casting of pure tin and decreased as the germanium content was increased. There was a great decrease in rate in the case of the castings containing zinc. This probably was attributable to the fact that the gray tin was being produced in a tin-zinc combination rather than in pure tin. It is interesting to note that, in the case of the tin-germanium combinations, those which had the greatest tendency to produce gray tin spontaneously were the ones which had the lowest rate of spread.

The steel sheet coupons were electroplated with iron so that the tin coating could not come into contact with the nonferrous constituents present in the steel. These might possibly have had some effect on the results of the experiments.

It will be observed that in general the time to spontaneous appearance tended to decrease as the germanium content was increased and as the transformation temperature was lowered.

It is important to note that the values of m and of time elapsed before spontaneous appearance probably would have been somewhat different if tin of a different composition had been used in producing the various castings and coatings.

It has been known for a considerable length of time that gray tin, when placed in contact with white tin under suitable conditions, causes the formation of gray tin on the latter. However, it is rather unexpected that a different element, such as germanium, behaves as an inoculant in a similar manner. In this connection it is interesting to note that germanium and tin are quite close together in the same group (IV) of the Periodic Table, and that the properties of germanium are somewhat similar to those of gray tin. For instance, they both crystallize in the cubic system, whereas white tin crystallizes in the tetragonal system.

In passing it may be noted that Goryunova recently reported that she had been unable to produce gray tin by inoculation with germanium (5).

CONCLUSIONS

Perhaps the most important conclusion to be drawn is the fact that white tin may be transformed into gray tin, at a suitable temperature, when the former (a) is in contact with elementary germanium; (b) is in contact with aqueous solutions in which certain germanium compounds have been dissolved; and (c) contains a certain proportion of germanium in the form of an alloy. Further, the rate of spread of gray tin in tin castings and coatings depends to a considerable extent upon the amount of germanium present and the transformation temperature.

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CONCLUSIONS

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2. [illegible]

3. [illegible] Eng. Chem. [illegible]

4. [illegible] Data for [illegible] England [illegible].

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