Tin Pest, A Review

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Abstract

With the transition to high tin solders, and 100% tin finishes, some concerns have been raised about the possible occurrence of "Tin Pest". This paper reviews the historical and recent data collected on this phenomenon. No attempt has been made to collect and explain thermodynamic data. Various myths are either explained or discounted, including one about "Napoleon's buttons". All linear rate data that could be found is included. A correlation with atomic radii of elemental additives is also expounded. A summary of analytical techniques which can be used for examining the results of this transformation is also included.

History

Only thirty-three elements have one solid form. An allotrope is by definition: an occurrence of an element in two or more forms in the same state[1]. In the range -40 to 60°C and 1 atmosphere of pressure there are only 6 elements that have more than one thermodynamically stable allotropic form: C, Ce, P, S, Sn and Yb.

Tin exists in two allotropic forms – the normal "white" tin (β tin), which has a tetragonal structure and alpha or "gray" tin which has a cubic structure and is usually seen at temperatures below the transition temperature of 13.2°C. The CRC Handbook of Chemistry and Physics[2] also notes that some people claim a third form between 162°C and 183°C, but this is not widely accepted.

Tin pest or tin plague has been known for centuries. Tin pest has been well known in the north of Sweden as the Sámi people spin thread from tin to decorate their clothes[3]. They add a few percent silver to retard the pest formation. The cases of it affecting pipe organs in medieval cathedrals and being ascribed to Satan are legendary[4]. It was also noted in pre-modern museum display cases, that if one piece of tinware "caught the disease" it would spread to other pieces in the same display case[5]. There was no central heating in those days and it would be quite common for these display cases to reach temperatures at or below 10°C. Other instances of archeological/conservation studies dealing with tin pest are found in references[6-9].

Recently there has been published a fairly popular book called "Napoleon's Buttons: How 17 Molecules Changed History", by P. Couteur and J. Burreson[10] of British Columbia. In this book they make, or remake the claim, that one of the reasons for the defeat of Napoleon's Grande Armeé in Russia (See **Figure 1**.) was that his soldiers had tin buttons. The argument is that in the cold of the Russian winter the normal, white tin turned to gray tin (tin pest), which has no structural integrity and as a result the soldiers could not keep their coats closed and this facilitated their freezing to death.

Figure 1 - Marshal Michel Ney Leads the French Rearguard in Russia

This scenario is highly unlikely for at two reasons. First, most of Napoleon's armies (not his Egyptian expedition at least) had previously spent considerable amounts of time in temperatures below 13.2°C, the transition temperature of tin. Even if one makes the argument that tin pest is more likely to occur at around -30°C, certainly several of Napoleon's armies spent considerable time slogging through the Alps and other mountains of Europe for weeks or months on end. No mention of this supposed problem has come to light from these forays into cold climates.

Virginia Shaw Medlen in her history of the Irish volunteer unit of Napoleon's forces "Legion Irlandaise (Napoleon's Irish Legion) 1803 – 1815"[11] states: "Buttons were gold for officers and brass for other ranks." Some brasses contain tin (1% tin is common for certain types), but they certainly did not contain 100% tin or even the tin concentration levels of modern tin/silver/copper (SAC) alloys, all of which contain at least 85% tin.

Also, the following quote[12] has been found: "Now, 183 years later, the splendid museum in Vilnius displays many objects relating to the Napoleonic adventure. What's this button, made of an alloy of copper and tin, stamped '61? It comes from a blue uniform jacket, almost certainly that of a Dutchman. For the 61st Line Regiment was made up largely of (mostly unwilling) conscripts from the Netherlands."[sic]

And from militaryheritage.com[13] one can buy buttons (presumably replicas) of the era of Napoleon. Nowhere in the listing of the button compositions of Napoleon's troops is there a mention of any military units that used tin buttons. The buttons were all pewter, even for officers. The only difference was whether the plating was non-existent, brass, copper (for soldiers) or silver or gold plated (for officers). See **Table 1**. It is somewhat ironic that pewter is a high tin alloy that in many early forms contained lead. The modern version contains about 91% tin, 7.5% antimony and 1.5% copper.

Table 1 French Regimental Buttons

Régiment	Soldat		Officier	
	Grand	Petit	Grand	Petit
La Garde Impériale			G	G
La garde Royale Italienne	P	P	S	S
2e Cuirassier	P	P	S	S
3e Cuirassier	P	P	S	S
L'infantrie de ligne (1792-93)	B	B	G	G
2e Régiment de ligne	B	B	G	G
3e Régiment de ligne	B	B	G	G
93 Léger	P	P	S	S
21e Régiment de ligne	B	B	G	G
37e Régiment de ligne	B	B	G	G
96e Régiment de ligne	B	B	G	G
3e dragon	P	P	S	S
16e dragon	P	P	S	S
L'artillerie à pied	B	B	G	G
L'artillerie (1793-94)	B	B		
Le 8e régiment d'artillerie à pied	B	B		
L'artillerie de la Marine		C		G
État-major			G	G
Commissaire de Guerre			S	S
Maréchal			G	G
Génie			G	

P = Pewter
B = Brass plated pewter
C = Copper plated pewter
S = Silver plated pewter
G = Gold plated pewter

There is also a legend that an official of Russia was executed after a trainload of tin bullion came into St. Petersburg and all that was found was a pile of black dust. He was believed to have made a switch and was killed for his crime. This may have been an embellishment of the recorded incident of tin ingots stored in that famed city that transformed one winter, but were restored to white tin just by melting the powder[14].

There is an 1899 reference[14a] to the transformation occurring in Sn5.06Pb0.59O with "traces" of copper and iron in the mix. If true, this is somewhat disturbing, as most references that deal with the change say that very small amounts of lead, much less than 5%, are enough to inhibit the transformation.

However, perhaps this was offset by the presence of the copper and iron, both cubic like gray tin, and/or the formation of cuprite (Cu_2O) and/or magnetite (Fe_3O_4) which are also both cubic. More will be said on this later in the paper.

Recent Work

Another legend is that Captain Scott's expedition died because their food was spoiled due to the kerosene cans stored on top of the food leaked when the solder joints underwent the white to gray tin transformation. However, cans recovered in 1957 showed absolutely no signs of the transformation, even after 46 winters of temperatures certainly in the range of -30 to -40°C[15]. It is mostly likely that they failed because of poor workmanship (not adhering to IPC workmanship standards).

White tin has all the characteristics of a metal. However, gray tin is metalloid in character. Not as many properties of gray tin are known, but one that is known is its resistivity. The resistivity of gray tin at 0°C is 300 micro-ohm-cm, while that of white tin at 20°C is 12.6 micro-ohm-cm[16]. This (increased resistivity of gray tin) alone would be enough to cause some circuits to fail.

The transformation from white to gray tin also exhibits a density change from 7.30 g/cc to 5.75 g/cc. This resulting increase of about 27% in volume change in going from white to gray tin has catastrophic effects on the physical integrity of the tin articles. Gray tin usually exists as a black powder; however, crystals of up to 2 mm in length are known[17]. There was a big push to try and produce crystals of the material in the 1950's because of the semi-conductor properties of gray tin.

Table 2 highlights the elemental/compound addition results of much of the very interesting work done with regards to the initiation of the transformation. It should be pointed out that in a previous paper[34] a similar table did not differentiate between the speed of nucleation or the subsequent wholesale transformation from white to gray tin. Even now it is not completely clear if the elements listed from reference 16 are in reference to reaction initiation or reaction rate after initiation. Most of the work cited was done between 50 and 100 years ago.

Table 2 Factors Affecting the Initial Transformation of Tin

SPEEDS TRANSFORMATION White -> Gray Transition	RETARDS TRANSFORMATION White -> Gray Transition
Mg, Zn, Co, Mn Te [16]	Bi [16,19-21,22a]
Al [16,17]	Sb [16,17,19-21,22a]
Ge [16,22]	Pb [16,19-21,22a]
Cold work + Mg [19-21]	Au [16,19-21,22a]
Cold work + Zn [19-21]	Cd [19-21,22a]
Cold work + Co [19-21]	Ag [16,19-21,22a]
Cold work + Mn [19-21]	As [17]
Cold work + Al [19-21]	In [17]
Cold work + Te [19-21]	
Si [18a]	Ni [16]
CdTe [21a, 22]	
InSb [22]	
Cold working the tin [19-21,23,24]	Annealing [19-21,23]
Reactor irradiation [25]	Surface oxidation [19-21,23]
Certain solutions [22,24,25]	Slow growth of initial white tin crystal [28]

It is tempting to surmise that cold working, radiation and the solutions mentioned in Table 2 result in vacancies in the tin crystal structure, which somehow facilitates the transformation. Conversely, surface oxidation could possibly fill surface imperfections and also prevent contact with tin pest "seeds". Slow crystal growth would help ensure a crystal structure with fewer defects. It is unclear in Becker's paper[18] whether he is referring to initial transformation or reaction rate when he discusses the Russian work where they applied high pressures. High pressures would of course shift any gray-white equilibrium towards white tin because white tin occupies less volume/gram.

Also, the information available is not devoid of contradictions either. Reference 16 claims nickel is a retarding agent while references 19 – 21, 22a and 23 say it has little or no effect. Sometimes the differing observations are the result of different concentrations. This may also be due to the interaction of subtleties caused by other impurities in the tin.
The above references made the same claim for iron, yet reference 14a said a tin/lead sample with some iron in it showed tin pest behaviour.

More recently, Plumbridge et al.[29] have sounded the alarm bells for the possibility of tin pest being a problem for lead free solders. They have seen the formation of the cubic form of tin in the tin/copper alloy Sn99.3/Cu0.7 after prolonged storage at low temperature.

Certainly there have never been any widely reported cases for tin/lead solders of 50/50, 60/40, 63/37 or even 80/20, 90/10 or 95/5 Sn/Pb showing signs of tin pest. It is therefore safe to say that addition of at least 5% lead to tin retards or eliminates the formation of gray tin. A page devoted to MIL & NASA prohibitions on the use of pure tin shows that alloying with 3% lead is specified in many cases[30]. This has as much to do with worries over tin whiskers as tin pest.

This transformation is also commonly prevented/retarded in modern tin casting and plating by alloying with small amounts of antimony or bismuth. The percent additions needed varied with the reference source, but amounts as small as 0.10 - 0.26 % antimony are claimed to prevent pesting. Bismuth is said to have the same effect at only 0.004%[17].

“Bad” ingredients (e.g. Mg, Mn, Fe, Co, Zn, Hg, Al, Si, Ge) increase the relative stability of gray tin vs. white tin. Some, like Ge[31], Hg[32] and Si[18a], allow gray tin to exist above the usual transformation temperature.

The author of reference 18 points out that the alpha to beta transformation for tin is not unique, but that it takes place more or less under STP (standard and atmosphere) conditions. **Table 3** from the above reference shows the relationship of related cubic elements and the pressure necessary to make the transition to the tetragonal structure.

Table 3 - Pressure Needed to Transform Cubic Allotrope to the Tetragonal Form

Element	Critical Pressure (bar)
C (Diamond)	23×10^6
Silicon	12×10^4
Germanium	8×10^4
Gray Tin	1

One area of considerable interest is the speed of the transformation. **Figure 2** and **Table 4** summarize the linear transformation rate data collected for this paper. It is immediately obvious from the figure that the rate of transformation decreases with increasing overall contamination. Just the data for the pure tins – no added impurities is shown in **Figure 3**. There is one point off the general trend and that is for a tin with 0.02% lead.

The addition of aluminum or gallium at first increased the rate of transformation, but larger amounts (0.1% and above) actually retarded the allotropic change. Arsenic slowed the change for either concentration tried. Antimony also retarded the change, but certainly did not stop it when at a concentration of only 0.1%. Indium was even more effective.

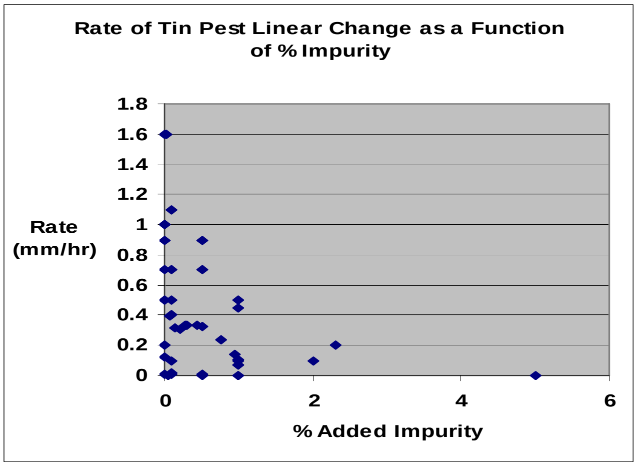

Figure 2 - Linear Rate of Transformation of White to Gray Tin at -30C to – 50C With or Without Added Impurities

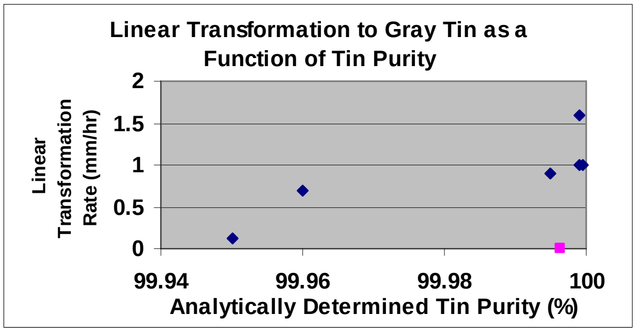

Figure 3 - Rate of Transformation of "Pure" White Tin at -30C to – 50C

Work by researchers at Nihon Superior was recently published[33]. Like others before them, they showed 99.9% tin and solder alloys made with it do not transform. Nine per cent zinc in 99.99% tin would suppress tin pest for 180 days at -45°C, but it did not stop the transformation if the alloys was placed in direct contact with gray tin. Elemental additions of 0.01% to 99.99% tin by alloying in most cases did not stop the spread of tin pest when the mini-ingots were put in direct contact with gray tin for 30 hours.
Surprisingly lead was the only element that completely stopped the transformation. Previous work suggested that Bi would have also worked, especially over such a short period.

The order of best transformation retarder to worst was found to be: Pb>Bi>Ag>Zn>In>P>4N's tin itself >Au>Al>Cu> Ge> Ni>Sb>Ga>Fe. This is very interesting. In other studies already alluded to zinc was regarded as worse and gold as better. This work also shows Sb, Ni and Fe not to be neutral with regards to the transformation. This shows one must be careful in determining the context of the statements made.

Unfortunately this latest fine work was done in terms of rate of area transformation from multiple contacts with gray tin, so no direct comparison with the linear rates in earlier work can be made.

It would be very interesting if the work was extended by repeating it with 0.1% additions of the same elements. To emphasize the importance of knowing more about the concentration of the added element, **Figure 4** from Smith's work[18] shows that the effect of the added element does not result in a monotonic increase or decrease in the rate of transformation. This is somewhat different than previous work of Trumond and Kawalchik who found a linear decrease in transformation rate of -0.10 +/- 0.01 mm/(hr wt %) from 0.36 mm/hr at 0.2% weight addition of germanium to 1% weight per cent germanium.[18b]

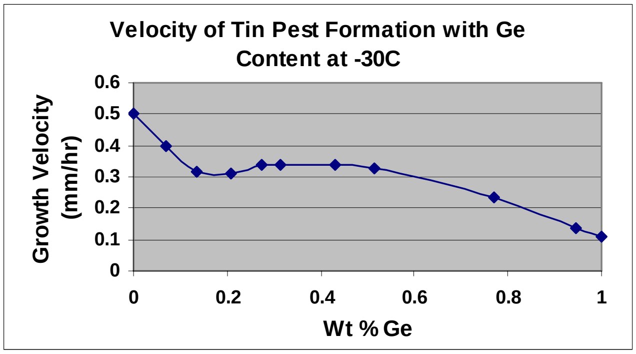

Figure 4 - Variation in β->α Velocity with Ge Content at -30C[18]

Attempts were made by the authors of ref[34] to cause the transformation at room temperature, 4°C, -4°C and -42°C of:

1. NEMI SAC alloy (normal tin purity) in the shape of discs (25 mg)
2. Eutectic tin/zinc in the shape of discs (25 mg)
3. Pure tin metal foil (99.99%)

- (All were bought from the Indium Corporation of America).

This only succeeded for the pure tin samples, impregnated with Si dust and stored at -42°C and -4°C. Transformation was known to have occurred because the shiny tin foil was replaced by a black powder. For -42°C the change occurred within a few months, but for samples stored at -4°C, it took about a year and a half.

Table 4 - Linear Transformation Rates for Pure Tins and Those with Intentionally Added Impurities [a,b,c,d]

	mm/hr
Tin A + 1.0% In	0
Tin A + 1.0% Sb	0
Tin D + 0.5% Bi	0
Tin D + 0.05% Sb	0
Tin F + 5% Te	0.0004
Tin C 99.99963%	0.007
Tin D + 0.1% Sb	0.01
Tin F + 0.5% Mg	0.01
Tin A + 0.1% In	0.019
Tin D + 0.1% Bi	0.02
Tin A + 1.0% Ga	0.066
Tin A + 1% Pb	0.0705
Tin E + 2.0% Cd	0.095
Tin A + 0.1% Sb	0.1
Tin A + 1.0% Al	0.1
Tin I + 1% Ge	0.11
E, Banka tin 99.95	0.125
Tin I + 0.95% Ge	0.14
Tin F + 2.3% Te	0.2
Kahlbum tin = D	0.205
Tin I + 0.77% Ge	0.24
Tin I + 0.21% Ge	0.31
Tin I + 0.14% Ge	0.32
Tin I + 0.51% Ge	0.33
Tin I + 0.27% Ge	0.34
Tin I + 0.31% Ge	0.34
Tin I + 0.43% Ge	0.34
Tin I + 0.07% Ge	0.40
Tin A + 0.1% As	0.4
Tin A + 1.0% As	0.45
Tin A + 0.1% Al	0.5
Tin F + 1% Te	0.5
Tin I [unknown]	0.5
Tin H 99.96%	0.7
Tin F + 0.5% Se	0.7
Tin F + 0.1% Te	0.7
Tin A 99.9995	0.9
Tin F + 0.5% S	0.9
Tin F 99.9996%	1
Tin G 99.999%	1
Tin A + 0.1% Ga	1.1
Tin A + 0.025% Al	1.8
Tin B + 0.025% Al	1.6
Tin B 99.999+ %	1.6

a-d) ref. 16, 17, 17a, & 18

A recent review[16] includes a small section on the mechanism of the transformation. In this section the authors repeat an earlier statement that the transformation cannot be martensitic in nature because of a lack of orientation relationship between the unreacted white tin and the transformed gray tin. However, this disagrees with statements made by Smith[18] and Ewald[35]. Also, Ojima and Takasaki[36] have shown by high-resolution electron microscopy that the (001) plane of gray tin is parallel to the (001) plane of white tin and that the [211] direction of gray tin is nearly parallel to the [010] direction of white tin. Based on their observations, they too believe the transformation is martenistic in nature.

Table 5 shows the elemental crystal symmetries and atomic radii[37] of various elements. The present author[34] sorted the data by crystal symmetry and/or then radii size in an attempt to find a relationship to the propensity of various elements to favor the formation of tin pest. This did not produce any clear trend, but sorting by the ratio of the radius of white tin/radius of other elements does show a trend.

Table 5 - Elemental Crystal Symmetries, Radii[37] and Radii Ratios with White Tin

Element	Crystal symmetry	Structure symbol	Metallic radii	Sn radius /other
C	fcc	A4	0.91	1.78
Ni	fcc	A1	1.24	1.31
🟦 Co	hex	A3	1.25	1.30
Fe	bcc	A2	1.26	1.29
🟧 Cu	fcc	A1	1.28	1.27
🟦 Si	fcc	A4	1.32	1.23
🟦 Mn	bcc	A12	1.35	1.20
🟦 Ge	fcc	A4	1.37	1.18
🟦 Zn	hex	A3	1.38	1.17
🟦 As	rhom	A7	1.39	1.17
🟦 Ga	orth	A11	1.41	1.15
🟦 Te	hex	A8	1.42	1.14
🟦 Al	fcc	A1	1.43	1.13
▥ Ag	fcc	A1	1.44	1.13
▥ Ti	hex	A3	1.45	1.12
▥ Au	fcc	A1	1.46	1.11
▥ Sb	rhom	A7	1.59	1.02
🟦 Mg	hex	A3	1.60	1.01
🟦 Hg	rhom	A10	1.60	1.01
▥ Sn (white)	bct	A5	1.62	1.00
▥ In	bct	A6	1.66	0.98
▥ Bi	rhom	A7	1.70	0.95
▥ Cd	hex	A3	1.71	0.95
▥ Pb	fcc	A1	1.75	0.93
Sn (gray)	fcc	A4		

Legend
⬜ effect unknown or neutral
🟧 suspected
🟦 favors transformation
▥ inhibits transformation

Elements that are said to generally favor Tin Pest are in blue (e.g. Al, Si and Zn) and those that retard it are in green and black stripes (e.g. Sb, Bi and Pb). Copper is highlighted in orange in the table, as it usually is stated to not influence the transformation at all. However, the recent British work (0.5% Cu @ -18°C) and that of Nihon Superior (0.01% @ -45°C) has shown otherwise. Similar statements have been made about the "neutrality" of nickel and iron. More work is warranted.

In most cases, the tin radius/other element radius ratio must be above 1.13 for the added element to have an effect. It is interesting to note that both aluminum and silver have the same ratio, but each is considered to be on opposite sides of the "fence". The author of reference[17] notes that 1% aluminum slows the linear transformation rate by a factor of 5, over that of 0.5%. No explanation can be offered at this time for the propensity of magnesium and mercury to favor the transformation.

How does one tell the difference between white and gray tin, other than by color? Several methods have already been alluded to, with x-ray diffraction techniques being the first ones to come to mind.

These would include regular XRD, single crystal x-ray crystallography[38, 39], and TEM-based methods[36]. **Figure 5,** from this authors' work mentioned above, shows green highlighted XRD peaks (~28.5° and 47.3°) due to Si, the small red ones (31°, 32°, 44° and 45°) are due to white tin and the blue ones (23.8° and 46.4°) are due to the gray tin produced by the experiment. The Si peaks are so large compared to the gray tin peaks because of the high level of crystallinity of the Si, compared to the gray tin.

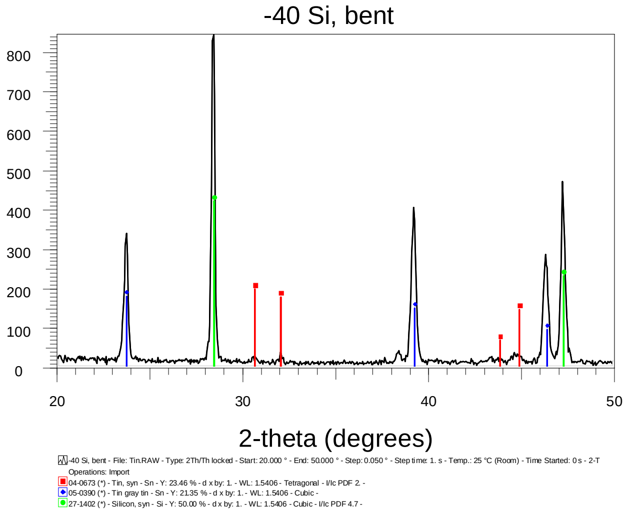

Figure 5 - XRD Pattern of the White Tin Transformation to Gray Tin in the Presence of Si Powder

One might be able to tell the difference by conductivity. Certainly this should be easy for any monolithic piece of white tin, but since gray tin is often in the form of a powder this would not be possible. Crystals of gray tin are known[17]. It should also be possible to tell the difference using a thermal mechanical analyzer (TMA) where one could bring the temperature up from -40°C to room temperature and measure the change in expansion. Obviously for white tin it should only be due to normal thermal expansion, while there would be a dramatic decrease in volume if gray tin changed to white tin.

A very simple chemical means of telling them apart is to simply put the tin in concentrated hydrochloric acid. White tin will form Sn (II), while gray tin will form Sn (IV). Standard tests to tell the two oxidation states of tin apart can then be used.

It should be possible to tell the two types of tin apart by vibrational spectroscopy. However, since most infrared spectrometers are only fitted with sodium chloride or potassium bromide optics, it is not normally possible to obtain a spectrum for such a heavy element. The spectrometer would have to have Mylar optics and be nitrogen purged. It would also be important to grind the sample at perhaps liquid nitrogen temperature, as grinding at higher temperature produced enough frictional energy to partially convert a sample of gray tin[9].

Another possibility would be to use the complimentary technique - Raman spectroscopy. One would think that cooling the sample such that the heat of the laser did not result in a conversion of the sample from gray to white tin would be necessary, but not enough heat is generated to cause enough of a transformation (if any) to limit gray tin spectral capture.[40] A small Raman peak at 196 cm^{-1} (polycrystalline, 297K) or 199 cm^{-1} (single crystal, 77 K) has been obtained for gray tin. A room temperature spectrum of white tin shows a peak at 128 cm^{-1}.[41]
One could try Mossbauer spectroscopy, but since it is not possible to tell the difference between such different but related compounds as SnO and SnO_2, it probably not a good choice. Any technique that involves heating the sample, like mass spectroscopy or secondary ion mass spectroscopy (SIMS) is also not going to work.

Tin has two isotopes with a nuclear spin of ½. Isotopes ^{115}Sn and ^{117}Sn have natural abundances of 7.68 and 8.59%, respectively[42] and high enough relative sensitivities that there is quite a body of work on tin nuclear magnetic resonance (NMR). Since the bonding in gray tin (covalent) and white tin (metallic) are so different, this technique theoretically should work. However, NMR cannot be used for either metallic or semi-conductive solid samples, so this technique is also eliminated.

There are several techniques used for surface analysis that might be applicable to an examination of the tin transformation. Electron energy loss spectroscopy (EELS) has been a useful tool to study electronic structure of molecular films even at the submonolayer level. It could be used to look for the first evidence of gray tin formation. It has been used for looking at semiconductors.[43] Rutherford back scattering might work, as, already mentioned, the bonding of the atoms are different in the two allotropes.[44] And of course there is also Photoelectron spectroscopy or ESCA.[45] However, "sputtering can introduce chemical state changes just due to the sputtering process....so we usually do not recommend any sputtering when trying to obtain chemical state information."[46]

Conclusions

- There is a large amount of research that has already been carried out in the area of the tin allotropic transformation. This should be carefully studied before undertaking any major new work.
- Just as in the case of tin whiskers, physical, as well as the chemical environment is important with regards to this phenomenon.
- Nothing favors the transformation from white to gray tin more than the purity of the tin itself.
- Seeding with gray tin is the most effective way to start the transformation.
- Previous work shows that the rate of transformation is controlled not only by what impurities are present in the tin, but also by how much is present.
- Additional elements were found that made the speed of transformation faster when the white tin was in contact with gray tin, but if the white tin was not inoculated, then usually the fastest rate was that of ultra-pure tin itself. Addition of certain concentrations of aluminum may be an exception.
- There are still unanswered questions about the addition of some elements.
- Even if 4N tin was used, it is likely that the dissolution of the elements from pad and component termination finishes would be enough to greatly retard tin pest formation.
- Identification of tin pest for what it is, is not experimentally easy in a system where there are other possible causes of normal tin corrosion.
- It appears that atomic size is a very significant, but not the only factor, in determining whether an element is deemed to favor tin pest formation.
- XRD is the primary technique for determining the presence of tin pest.

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