Thomas, *et al.*,[7] assigned this type of structure to boron nitride prepared from urea–boric acid and ammonia. It now appears that boron nitride derived from a number of different routes possesses the turbostratic structure. In Table IV X-ray data reported by others for boron nitride prepared by five different methods are compared with data for samples prepared by the new routes. The interlayer spacings and the L_a and L_c dimensions which represent the width of the graphite-like layer and the thickness of the parallel packet of layers, respectively, are used to define the turbostratic phase.[11] Values of $d(002)$, L_a, and L_c for the turbostratic, mesographitic, and graphitic phases are shown for route 1. Routes 2–5 yield products which closely resemble the turbostratic phase. Route 6 yields products which more nearly resemble the mesographitic and graphitic phases, depending on temperature of reaction. In the latter case, it would appear that, if a lower reaction temperature could be used, a more random structure approaching the turbostratic phase would result.

Boron nitride prepared *via* these routes undoubtedly differs in the ease of conversion to graphitic boron nitride. As pointed out by Thomas, *et al.*,[7] both boric oxide and boron nitride seed crystals play important roles in this transformation. Tagawa and Ishii[12] also indicate that boron nitride prepared in a solid–gas reaction crystallizes more readily than boron nitride formed in the gas phase.

(12) See footnote *b* of Table IV.

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The Divalency of Tin Ions Formed during Anodic Dissolution and the Behavior of the Tin Anode[1]

BY M. E. STRAUMANIS AND M. DUTTA

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Tin was found to form solely Sn^{2+} ions when dissolved anodically without the use of an external current from tin amalgam in aqueous solutions of HCl, H_2SO_4, $HClO_4$, H_3PO_4, HNO_3, and HF. Darkening of the surface of a solid tin anode was observed during electrolytic dissolution up to current densities of 1200 ma cm^{-2} in HCl, H_2SO_4, and $HClO_4$, but there was no spalling of particles. The black entities protruding from the anodic surface were in contact with the surface of the anode and consisted of metallic tetragonal tin. They were formed owing to the uneven electrolytic surface attack of the tin anode.

Introduction

In 1916, Newbery,[2] working on the anodic polarization of tin in sulfuric acid, observed the formation of a black coating on the anodic surface. The same observation was also made by Vaubel while dissolving tin anodically in hydrochloric acid.[3] He noted a black powder on the anode which dissolved very slowly even in concentrated acid. Therefore, it was assumed that the powder represented a peculiar modification of the metal. Jeffery,[4] electrolyzing a potassium oxalate solution with a tin anode, found that it became covered with a fine black adherent film at low current densities which spalled at higher ones.

Similar observations were also made during anodic dissolution of tin in an NaOH solution by Vallesi,[5] who found a black, powdery tin layer on the anode. The same experiments were later repeated by Nakai and Kato.[6]

The anodic formation of a black layer on the dissolving tin resembles a phenomenon called partial "surface disintegration" which has been frequently observed in our laboratories. A spalling of finest metallic particles occurs at the dissolving anode. The particles are recognizable as such only at high optical magnifications. Surface disintegration occurs also when a metal is simply dissolved in an acid, *e.g.*, Be in HCl[7] and Fe in H_2SO_4.[8] Partial disintegration of other metals can nearly always be enforced by anodic dissolution. It could thus be shown that the metals beryllium,[9] magnesium,[10] gallium,[11] indium,[12] aluminum,[13] thallium,[14] and zinc[15] partially disintegrate when dissolved anodically. The possibility of disintegration (metallic chunk formation) during corrosion

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(1) Extract from the thesis submitted by M. Dutta to the Graduate School of the University of Missouri at Rolla in partial fulfillment of the requirements for an M.S. degree.

(2) E. Newbery, *J. Chem. Soc.*, **109**, 1066 (1916).

(3) W. Vaubel, *Ber.*, **57B**, 515 (1924).

(4) F. H. Jeffery, *Chem. Abstr.*, **18**, 2998 (1924).

(5) E. Vallesi, *Ann. Chim. Appl.*, **27**, 157 (1937).

(6) T. Nakai and M. Kato, *Kogyo Kagaku Zasshi*, **62**, 1488 (1959).

(7) M. E. Straumanis and D. L. Mathis, *J. Less-Common Metals*, **4**, 213 (1962).

(8) M. E. Straumanis, G. E. Welch, and W. J. James, *J. Electrochem. Soc.*, **111**, 1292 (1964).

(9) M. E. Straumanis and D. L. Mathis, *ibid.*, **109**, 434 (1962).

(10) M. E. Straumanis and B. K. Bhatia, *ibid.*, **110**, 347 (1963).

(11) M. E. Straumanis and K. A. Poush, *ibid.*, **111**, 795 (1964).

(12) M. E. Straumanis and R. L. Martin, *Z. Anorg. Allgem. Chem.*, **334**, 321 (1965).

(13) M. E. Straumanis and K. A. Poush, *J. Electrochem. Soc.*, **112**, 1185 (1965).

(14) M. E. Straumanis and R. L. Martin, *Corrosion Sci.*, **6**, 765 (1965).

(15) W. J. James, G. E. Stoner, and M. E. Straumanis, Technical Report No. 4 to the Office of Naval Research, 1963.

of metals was discussed previously by Marsh and Schaschl.[16]

The relation of this disintegration with the valency of ions formed anodically is as follows: if disintegration of the metal is disregarded, a deviation from Faraday's law will be found in the sense that more metal than calculated will pass into solution. This deviation has been explained, *e.g.*, in the case of beryllium, as due to formation of lower than normal valency ions.[17]

It was therefore, of importance to investigate the black layer formed on tin during anodic dissolution and to state its nature. While this investigation was in progress, an article by Rumpel, Davidson, and Kleinberg[18] appeared which stated that tin dissolves anodically in the initial stage as univalent Sn^+ ion. In view of this, the present investigation was extended to check the possibility of Sn^+ ion formation, especially in strong acids.

Experimental Arrangement

The valency of the tin ions anodically formed in acidic solutions was investigated first. To exclude anodic disintegration phenomena, liquid tin amalgam was used as an anode, so that tin could pass into solution by its own free energy.

The analysis of the tin (Baker Analyzed high-purity product) was as follows: Sn, 99.996; Pb, 0.003; and Fe, 0.001 by weight. This metal was dissolved in mercury (triply distilled). All of the acids were of reagent grade.

The coulometric measurements were performed with a sensitive high-quality Weston direct-current milliammeter. A platinized platinum electrode served as a cathode.

The apparatus for dissolution of tin from its amalgam consisted of a small beaker containing the particular electrolyte in which a still smaller beaker could be submerged, holding 2–3 ml of mercury, as shown in Figure 1, inset. The electrodes were connected through a resistance and the milliammeter. The cell produced only a very weak current when the circuit was closed.

A piece of accurately weighed tin (20–40 mg) was dissolved in the mercury, Figure 1, inset. Then the circuit was closed, and the tin was dissolved anodically from the amalgam. The current, I, was read immediately and then in 1-min intervals until it dropped to zero. The readings were plotted against time, t, and the areas under the curves were measured with a compensating planimeter. The number of coulombs was calculated from these areas (It), and the weight, w, dissolved was calculated from

$$w = ItA/nF \tag{1}$$

where A is the atomic mass of Sn, F is 96,487 coulombs, and n is 2, the normal valency number of Sn. The valency V actually found was computed from

$$V = nw/w_0 \tag{2}$$

where w_0 is the amount of tin weighed in.

This simple procedure has the advantages: (1) no external emf is necessary and, therefore, no mercury can pass into solution faradaicly as long as tin is present in the mercury and no oxygen can be developed on the anode; (2) there is no need to exclude the oxygen of the air; and (3) analyses are not necessary. Oxygen does not influence the total amount of the electrons passing the milliammeter because the only efficient source of electrons is the Sn dissolved in the Hg. Oxygen, being an electron acceptor, could be effective only then, if it could catch the electrons of Sn *before* their entering the circuit. Hence, the reaction

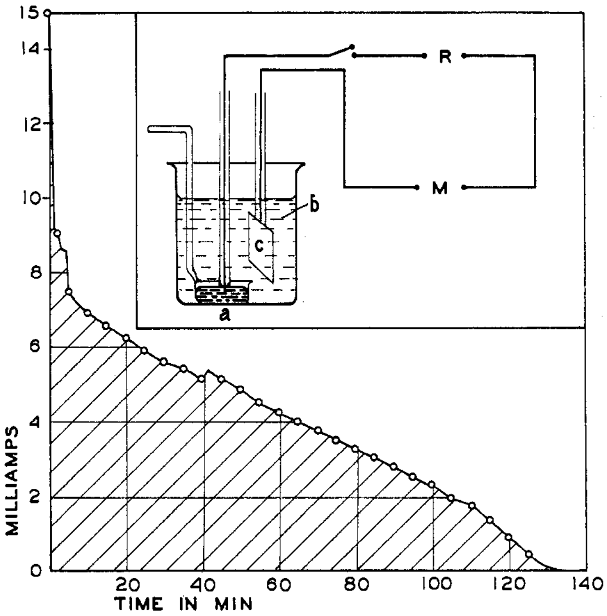

Figure 1.—Inset: Experimental setup for valency determinations by the amalgam-electrode method using only internal current: (a) Hg anode containing Sn (0.0196 g); (b) electrolyte (1.5 N $HClO_4$); (c) platinized Pt cathode; M, milliammeter; R, resistance box. Curve: Plot of current strength (produced by the Sn amalgam) *vs.* time (only every fifth minute is shown on the curve). Shaded area = 31.92 amp-sec which corresponds to 0.01963 g of Sn; valency (eq 2) $\simeq$2.01.

$$Sn + {}^1/_2O_2 \longrightarrow SnO \tag{3}$$

$$SnO + 2H^+ \longrightarrow Sn^{2+} + H_2O$$

should occur on the surface of the amalgam, outside the circuit. This is the reaction of self-dissolution and would result in an apparent decrease of the valency of Sn ions (more Sn would go into solution than according to Faraday's law, assuming $n = 2$). However, reaction 3 as well as the reaction

$$Sn + 2H^+ \longrightarrow Sn^{2+} + H_2 \tag{4}$$

did not occur, as shown in Tables I and II, where even the lowest valency numbers are within the limits of error. The reason is the nobility of Sn. Even in case of more active metals, such as Zn, reactions 3 and 4 can be neglected. However, they occur if the amalgam of the still more active Al is chosen as an anode.[18] Besides, the surface of the Sn amalgam is protected from the action of oxygen because, during its diffusion to the anode, it becomes consumed in the reaction

$$Sn^{2+} + {}^1/_2O_2 + 2H^+ \longrightarrow Sn^{4+} + H_2O \tag{5}$$

Thus, it is unnecessary to remove the air from the electrolytic cell.

In each experiment (Figure 1) no weighable amounts of Sn were left in the Hg after the current decayed to zero because always the same valency number was obtained (within the limits of error), regardless of whether the measurements were made with fresh Hg as a solvent or with a depleted one. Hence, no accumulation of Sn in Hg occurred in repeated measurements.

Results

Valency.—Table I gives the results in detail as to how the valency of Sn ions in hydrochloric acid was obtained (room temperature ~25°).

Table I shows clearly that within the limits of error only Sn^{2+} ions are produced, regardless of the number

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[16] G. A. Marsh and E. Schaschl, *J. Electrochem. Soc.*, **107**, 960 (1960).

[17] B. D. Laughlin, J. Kleinberg, and A. W. Davidson, *J. Am. Chem. Soc.*, **78**, 559, 560 (1956).

[18] M. L. Rumpel, A. W. Davidson, and J. Kleinberg, *Inorg. Chem.*, **3**, 935 (1964).

TABLE I

VALENCY OF Sn IONS GOING INTO SOLUTION FROM Sn AMALGAM IN HCl

[HCl], N	It, amp-sec	Calcd w, g	Input w, g	Δ, %	Valency no.	Av
6.0	43.68	0.02686	0.0265	+1.35	2.03	
6.0	45.99	0.02828	0.0280	+1.0	2.02	
6.0	36.66	0.02254	0.0222	+1.53	2.03	
6.0	40.26	0.02476	0.0248	−0.16	2.00	
6.0	54.16	0.03331	0.0331	+0.64	2.01	
6.0	66.215	0.04072	0.0409	−0.55	1.99	2.01
3.0	37.818	0.02326	0.0232	+0.25	2.01	
3.0	51.75	0.03182	0.0315	+1.01	2.02	
3.0	45.086	0.02773	0.0280	−0.97	1.98	2.00
1.0	26.745	0.01645	0.0165	−0.31	1.99	
1.0	27.76	0.01707	0.0171	−0.18	2.00	
1.0	14.52	0.00893	0.0088	+1.47	2.03	
1.0	40.845	0.02512	0.0252	−0.3	1.99	2.00
0.5	20.72	0.01274	0.0128	−0.71	1.99	1.99
						Av 2.00

TABLE II

VALENCY OF Sn IONS GOING INTO SOLUTION FROM Sn AMALGAM IN VARIOUS ACIDS

Electrolyte	Concn, N	Av Δ, %	No. of measurements	Av valency
H_2SO_4	18	−0.07	3	2.00
H_2SO_4	15	+0.5	4	2.01
H_2SO_4	6	+0.6	3	2.01
H_2SO_4	3	+0.3	4	2.01
H_2SO_4	2	+0.2	1	2.00
$HClO_4$	8	−0.03	5	2.00
$HClO_4$	4	−0.42	1	2.01
$HClO_4$	3	+0.1	5	2.01
$HClO_4$	1.5	−0.08	4	2.00
H_3PO_4	25	+0.02	4	2.00
H_3PO_4	17	+0.03	5	2.00
H_3PO_4	8.5	+0.4	3	2.01
HNO_3	1.0	−0.04	7	2.00
HNO_3	0.5	+0.45	5	2.01
HF	6.0	+0.5	8	2.01
HF	3.0	−0.5	3	1.99
				Av 2.00

of coulombs and the concentration of the hydrochloric acid.

In Table II, results are given for other acids as electrolytes using the apparatus of Figure 1.

Table II shows again that only Sn^{2+} ions were produced even in an oxidizing acid such as HNO_3. However, in this acid, the current of the cell (Figure 1) did not drop quite to zero (indicating that some mercury dissolved anodically when the tin became exhausted), but this residual current was subtracted from the total.

In all acids mentioned in Tables I and II, no dissolution (with the circuit open) of the liquid amalgam occurred (except to a slight extent in HNO_3) as could be concluded from the absence of gas evolution on the mercury surface. However, pure tin itself showed a slight self-dissolution rate even in 0.02 N nitric acid, about 0.00365 g cm^{-2} hr^{-1} (average of four tests). This was a further reason why tin amalgam and not pure tin was used for the valency determinations.

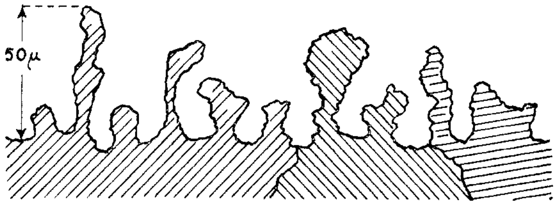

Figure 2.—Corrugated (fragmented) surface of an Sn anode after anodic dissolution. The figure is drawn on the basis of microscopic studies.

No attempts were made to dissolve the tin anodically in neutral solutions from the amalgam by the use of an external emf, because preliminary tests showed that either pure mercury or the tin amalgam in aqueous sodium nitrate developed a fine black dispersion even at low current densities (10 ma cm^{-2} and less) on the liquid anode. This black dispersion was also observed by Rumpel, *et al.*[18] It dissolved in 3 N hydrochloric acid and was found to be mercury.

Surface Fragmentation of the Anode.—Since in fairly concentrated acids (Tables I and II), tin dissolved only as the divalent ion Sn^{2+}, then how, using an external emf and a solid tin anode in neutral oxidizing electrolytes, are ionic valencies as 1.02 obtained?[18] It was mentioned in the introduction that some researchers observed a black deposit, which, at times, spalled off the dissolving tin anode.[2–6] This phenomenon, resembling very much the surface disintegration found for other metals,[8–16] was also observed for tin by the present authors, especially at high current densities (up to 1200 ma cm^{-2}). However, no spalling occurred although the black layer on the anode was slightly adhering and could be easily removed with a rubber policeman, even with a soft brush. After washing the black powder in water and acetone, it was examined microscopically. No resolution could be achieved at low magnifications. However, by using an oil-immersion objective, the presence of very fine metallic particles could be observed, similar to those found for iron or aluminum.[8,13] The presence of tetragonal tin in the black powder was confirmed by X-ray diffraction.

The solid tin anode turns black even at current densities as low as 5–10 ma cm^{-2} (in 0.5–9 N HCl). The blackening occurs at a much faster rate for increased current densities, and a yellowish stream of a tin salt solution is seen flowing down from the anode. Above 1000 ma cm^{-2} (in H_2SO_4) the black film is gradually replaced by a white one (SnO_2?). In perchloric acid, electropolishing occurs under the same conditions.

The black anodic surface, obtained after anodic dissolution in perchloric acid, was examined under the microscope at a magnification of 750×: particles extending from the metallic surface could be clearly seen. The distance from the particle tips to the surface varied between 5 and 60 μ as shown schematically in Figure 2. Thus, the tin anodes are not attacked evenly by the anodic dissolution process, but there are microscopic parts on the surface which resist greatly the dissolution reaction in accordance with previous observations.[3,4] Even after a short period of anodic attack, the anode surface may become corrugated. This process of roughening of the anode surface due to the uneven dissolution may be called "surface fragmentation."

Discussion

The explanation of the results obtained with a tin anode is possible if we assume that partial surface fragmentation occurs even at low current densities (the surface turns black) and that all of the tin particles present on the tin anode make good electrical contact (Figure 2). In such cases, when no breakdown of the extended tin protrusions occurs, the normal valency number of 2 for the Sn ions is found (*e.g.*, by Rumpel, *et al.*,[18] in sodium chloride, acetate, and tin chloride solutions and with tin amalgam in an arrangement as shown in Figure 1 where no anodic formation of particles and their dispersion in the electrolyte can occur). An apparent valency of less than 2 will be measured if some tin is lost and does not contribute to the faradaic current. Such a loss may occur at specific conditions which further the breakdown of the protrusions shown in Figure 2. For instance, oxidizing agents[18] such as sodium nitrate or potassium chlorate may produce oxide layers on the tin surface (eq 3), so that the protrusions (Figure 2) become thinner and lose their strength and elasticity at their thinnest parts and so that breakdown of the particles can easily occur, especially if intermittent current[18] is used which introduces some oscillations. The touch of the anode with even a soft brush causes breakdown of the protrusions, and, if their weight is not subtracted from the total weight of dissolved tin, the calculated valency of tin ions will be less than 2. The loss of tin particles may be further promoted in oxalate solutions.[4] Application of an external current to a cell having tin amalgam as an anode causes dispersion of the amalgam[18] which reduces the calculated valency of the tin ions.

The particle breakdown or disintegration process may be quite regular because very many particles are involved, and, thus, in a certain electrolyte at a certain current density, the same calculated lower valency of the tin ions (within the error span of several per cent) will be obtained.

Finally, the existence of tin grains with high resistivity toward the action of acids within a less resistive matrix may be explained by the differential concentration of impurities and imperfections within the metal during cooling: the purer and less imperfect areas may produce high-resistivity grains, so that anodic dissolution will nearly undermine them (see Figure 2).

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
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The Crystal Structure of Dimethyltin Difluoride. An Example of Octahedral Coordination of Tin[1]

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As part of an investigation of possible trigonal bipyramidal or octahedral coordination of tin, the structure of $(\mathrm{CH_3})_2\mathrm{SnF_2}$ has been determined. Dimethyltin difluoride forms tetragonal crystals in space group I4/mmm with $a = 4.24$ and $c = 14.16$ A and with two formula units per unit cell. The structure consists of an infinite two-dimensional network of tin atoms and bridging fluorine atoms with the methyl groups above and below the plane completing the octahedral coordination of the tin. The interatomic distances are Sn–C (2.08 ± 0.01 A) and Sn–F (2.12 ± 0.01 A). The crystal structure is the same as that of $\mathrm{SnF_4}$ except that the nonbridging fluorines in $\mathrm{SnF_4}$ are replaced by methyl groups in $(\mathrm{CH_3})_2\mathrm{SnF_2}$.

Introduction

The physical and chemical properties of $\mathrm{R}_x\mathrm{SnF}_{4-x}$ ($x = 0$ through 3) compounds are quite different from those of the corresponding bromides and chlorides. For example, the melting point of the fluoride is always much higher than that of the corresponding bromide or chloride, and the chloride and bromide are generally much more soluble in nonpolar organic solvents than is the fluoride. More specifically, $(\mathrm{CH_3})_2\mathrm{SnF_2}$ decomposes without melting at $\sim$400° while $(\mathrm{CH_3})_2\mathrm{SnBr_2}$ melts at 74–76° and $(\mathrm{CH_3})_2\mathrm{SnCl_2}$ at 90°.

It has been predicted[3] that dialkyltin difluorides should have octahedral coordination around tin with bridging fluorines. As a part of a study of possible trigonal bipyramidal or octahedral coordination of tin,

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[1] Research performed under the auspices of the U. S. Atomic Energy Commission.

[2] Department of Chemistry, University of Missouri, Columbia, Mo.

[3] I. R. Beattie and T. Gilson, *J. Chem. Soc.*, 2585 (1961).