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Observations of the Spontaneous Growth of Tin Whiskers on Tin-Manganese Alloy Electrodeposits

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The spontaneous growth of tin whiskers on electrodeposited tin-manganese alloy coatings has been observed. This growth is distinct from any previously reported whisker growth on either pure tin or other tin-based alloy electrodeposits. It has an extremely short incubation period of a few hours only, followed by a spectacularly rapid and profuse growth. During the whole period of whisker growth, the tin-manganese electrodeposits were found to be in a tensile residual stress state. This rules out the commonly accepted explanation of a compressive stress as the driving force for tin whisker growth.

Tin whiskers are very thin single crystals of β-tin [1] with a diameter of typically 1–5 μm. Their spontaneous growth on electrodeposited tin and its alloys during storage or usage have been known for over 50 years [2,3]. These filamentary growths were responsible for a large number of "shorting" failures [4] in key equipment, and are currently of particular concern to the electronics industry as it is forced, under both legislation and marketing pressures, to adopt pure tin or lead-free tin-based alloys [5] as alternatives to the standard, whisker-free tin-lead solders. However, the whiskering phenomenon on tin-based materials is not completely understood [6–11], while the extremely long incubation period to the formation of tin whiskers, typically months or even years [2], has to a large extent hindered fundamental investigations. In the present Letter, we report the discovery of the spontaneous growth of tin whiskers on a new alloy electrodeposit of tin manganese within a few hours of its deposition. The extremely short incubation period of this alloy system makes it an excellent subject for mechanistic studies, allowing the possibility of the elimination of tin whiskers through real-time study, a process until now thought to be impossible.

The electrodeposition of tin-manganese alloys from aqueous solution was difficult to achieve as manganese has a very negative standard electrode potential of −1.18 V with respect to the standard hydrogen electrode. Previously reported attempts [12,13] to electrodeposit tin-manganese alloys had limited success either due to the low cathodic current efficiency (CCE) of approximately 5% [12] or due to the co-deposition of hydroxide [13]. Fortuitously we managed to produce satisfactory tin-manganese alloy electrodeposits from a tin and manganese sulfate electrolyte containing boric acid and ammonium sulfate together with a nonionic surfactant and complexed with sodium gluconate. The solution was at pH 3.5 and room temperature, and there was no agitation. Samples of mild steel panels (25 × 40 mm) were first cathodically electrocleaned in an alkaline solution and then electro-

deposited with tin-manganese alloys up to approximately 8 μm coating thickness. The composition of the deposits obtained was examined using an energy dispersive x-ray analyzer incorporated in a field emission gun scanning electron microscope (FEG-SEM). It was found that with increasing applied current density the manganese content in the deposits increased from 0 (0.5 A dm^{-2}, CCE = 75%) to 18–23 wt % (1 A dm^{-2}, CCE = 65%) and finally plateaued at around 40 wt % (2–4 A dm^{-2}, CCE = 53%–61%). After electrodeposition, all the samples obtained were kept in an ambient environment for the investigation of tin whisker growth.

To determine the propensity of tin-manganese alloy electrodeposits to form tin whiskers, samples prepared at different current densities were examined shortly after electrodeposition and subsequently at daily intervals, using an optical microscope at a magnification of ×500. It was found that tin-manganese alloys deposited at 1 A dm^{-2} were most prone to whisker formation with an incubation period of less than 17 h. As shown in Fig. 1, shortly after
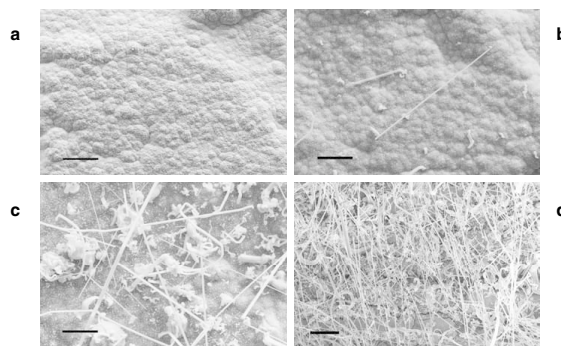

FIG. 1. FEG-SEM micrographs showing the growth of tin whiskers. The deposit surface was examined (a) shortly after electrodeposition (less than 1 h) and (b) after 17 h. Note the whiskers growing on the surface (c) after 1 week and (d) after 1 month. Scale bars: 1 μm (a)–(c) and 20 μm (d).

electrodeposition, the deposit surface was nodular in morphology and there were no whiskers or cracks observed [Fig. 1(a)]. 17 h later, many short and straight whiskers with a length up to 30–40 μm were observed on some areas [Fig. 1(b)]. With increasing storage time, new whiskers started to grow as indicated by the increased population density and surface coverage [Fig. 1(c)], while old whiskers maintained growth at a rapid rate. Within 1 week, many whiskers had grown to a length of approximately 100–300 μm, corresponding to a growth rate of at least 2–6 Å s^{-1}; this can be compared to typical reported growth rates of only 0.01–0.1 Å s^{-1} [8]. At this stage, some localized cracking, mainly around the root of whiskers, was observed. After 1 month, the whole deposit surface was fully covered by a large quantity of long whiskers together with a marked network of cracks [Fig. 1(d)]. For the deposits prepared at other current densities, the first observation of whiskers took approximately 15 d at 0.5 A dm^{-2}, while within the current density range of 2–4 A dm^{-2}, the incubation period varied from 2 to 3 d.

The incubation period was also a function of deposit thickness. The thinner the deposit, the shorter the time to the first observation of tin whiskers. For tin-manganese alloy electrodeposits prepared at 1 A dm^{-2}, tin whiskers were observed 7 h after electrodeposition on the surface of deposits with a thickness of 0.3 and 1 μm. For coatings of 4 and 16–24 μm, whiskers appeared after approximately 12 and 24 h, respectively. In addition, it was found that the most profuse tin whisker growth was found on deposits with a thickness of 4–8 μm. On thinner deposits (0.3–1 μm) the whisker population was much lower, while on thicker deposits (16–24 μm) the whisker population was high, but most of the whiskers were short in length. This characteristic is consistent with the result reported by Glazunova and Kudryavtsev [14].

Unlike the growth on other tin-based surfaces, the rapid formation of tin whiskers on tin-manganese alloy electrodeposits has not been found to depend on external conditions, such as the nature of the substrate material (e.g., mild steel, nickel undercoat on mild steel, copper, or brass). Similarly, pretreatment methods (chemical or electrochemical degreasing in an alkaline solution, or degreasing by acetone immersion only) and the thickness and surface roughness of the substrate had no effect. However, it seemed that a characteristic, rapid room temperature oxidation of the deposit surface was a precursor to the formation of tin whiskers.

Figure 2 shows the time sequence of the deposit appearance on separate coupons. Shortly after electrodeposition at a current density of 1 A dm^{-2}, the deposits obtained appeared silver gray with a few faint streaks formed on the surface due to hydrogen evolution [Fig. 2(a)]. The deposits soon became tarnished within a few hours mainly along those streaks, and the earliest observations of tin whiskers were always made in those preferentially tarnished areas [Fig. 2(b)]. After 1 week, the whole surface of the deposit
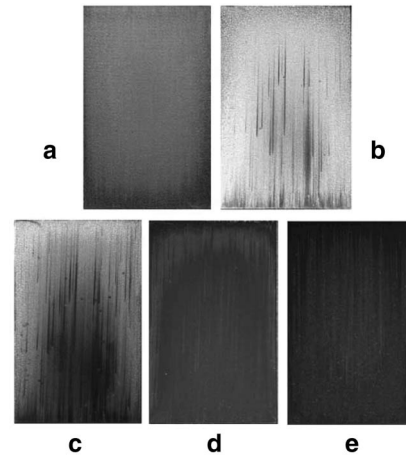

FIG. 2. Photographs of coupons showing deposit tarnishing during ambient storage (a) shortly after electrodeposition (less than 1 h), (b) after 17 h, (c) after 3 d, (d) after 1 week, and (e) after 1 month.

became dark gray due to tarnishing [Figs. 2(c)–2(e)], and this was accompanied by the growth of large quantities of tin whiskers as shown in Figs. 1(c) and 1(d).

The high population density of tin whiskers on tin-manganese alloys allowed us to track the whisker growth process by an x-ray diffraction method. Figure 3(a) shows the x-ray diffraction patterns recorded at different stages of storage of a tin-manganese alloy electrodeposit produced at 1 A dm^{-2}. The diffraction pattern of the alloy taken shortly after the electrodeposition indicates that it is predominately an intermetallic compound, MnSn$_2$. The weak and broadened peaks of MnSn$_2$ may be attributed to its small grain size. With an increase in storage time, some new diffraction lines appeared emanating from β-tin and accompanying the growth of tin whiskers. The intensity of these reflections for β-tin kept increasing while the reflections for MnSn$_2$ became weaker and eventually had completely disappeared into the background [Fig. 3(b)]. In 1952, i.e., one year after the first report on tin whiskers by Compton and Menizza [2], Faust and coworkers [12] also obtained similar x-ray diffraction results on their tin-manganese (55 wt %) alloy electrodeposits, but they did not mention the existence of any whiskers and believed that the alloy underwent a phase change on ageing.

The residual stress in tin-manganese alloy electrodeposits was measured using the bent strip method [15,16], to determine if the rapid growth of tin whiskers was due to a compressive stress, which is commonly accepted as the driving force for whisker growth [9,10,16]. For tin-manganese alloy electrodeposits, it is quite probable that a high compressive stress may have arisen from the adsorption of hydrogen in the deposits as a result of relatively low current efficiencies ranging from 51%–75%. However, it was found that, except for the deposit at 0.5 A dm^{-2} having a compressive stress (8 MPa), all the other deposits produced within 1–4 A dm^{-2} had a tensile
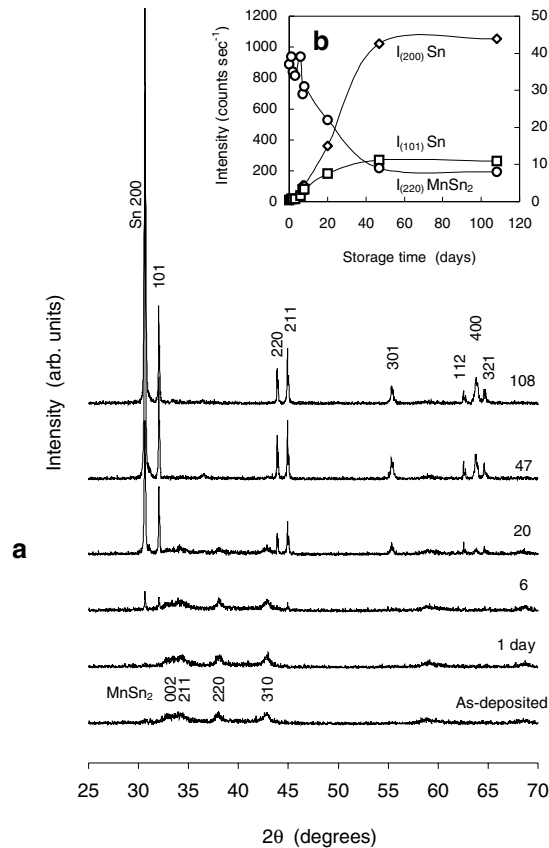
FIG. 3. Phase changes of a tin-manganese alloy electrodeposit during storage. The x-ray diffraction patterns were recorded with Cu Kα ($\lambda = 1.5406$ Å) irradiation in the 2θ angular range of $25°$ to $70°$. (a) X-ray diffraction patterns after different storage times as indicated on the right-hand side of the curves. (b) The variation with storage time in the intensity of different diffraction lines, i.e., (200) and (101) of tin, and (220) of $MnSn_2$. The curve for $MnSn_2$ is plotted on the secondary y axis on the right.

stress (6–29 MPa), as shown in Fig. 4. Contrary to the Lee-Lee result [16], the value of the tensile stresses showed a rapid increase and reached a maximum after 4–6 d ambient exposure. The rapid increase of the tensile residual stress may be a result of diffusion of the occluded hydrogen out of the deposit [17]. The decrease in the tensile stress after the maximum may be due to the surface cracking and the consequent stress relief. After nearly three months ambient storage, these tin-manganese alloy electrodeposits were still in a slightly tensile state. Therefore, the rapid formation of whiskers on tin-manganese electrodeposits did not follow the stress relief theories [9,10], in which the existence of a compressive stress is a prerequisite.

Although the accelerating factors to the growth of tin whiskers on tin-manganese alloy electrodeposits are still not known, the characteristics found with this peculiar whisker growth are invaluable. The extremely short incubation period and the rapid growth rate of tin whiskers would enable real-time investigations into the nucleation and growth process which were impractical in the past. As
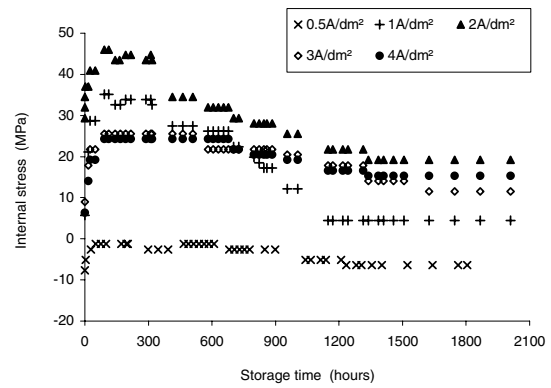

FIG. 4. Residual stress of tin-manganese alloy electrodeposits as a function of storage time. The positive (negative) values of stress represent tensile (compressive) stress states.

the growth is a spontaneous process and there were no external driving forces applied, there is a much better chance to identify the real cause for whisker growth, which would otherwise be masked if any acceleration method, such as a compressive stress or thermal cycling [4], was applied. The rapid and marked room temperature oxidation of tin-manganese alloy deposits will also allow us to determine if the growth of tin whiskers on tin-manganese alloys was a recrystallization process initiated by the selective oxidation of manganese, thus providing new evidence to the arguable relevance of oxide formation to the formation of tin whiskers [9]. Finally, the tin-manganese alloy deposits were prepared by an electrodeposition technique; this therefore presents a potential for the development of whisker mitigation strategies through electrolyte modification.

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