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Investigation of hydrogen embrittlement of Sn–Al alloy during contact with water vapour

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Abstract The humid air induced processes of embrittlement of the Sn–Al alloy and hydrogen emission have been investigated. Using the secondary-ion mass spectrometry, X-ray, scanning electron microscopy and energy-dispersive X-ray spectrometry techniques it was found that the brittleness is caused by a failure of phase adhesion due to accumulation of hydrogen and formation of oxidized layers on phase boundaries during contact of the alloy with water vapour. Specific physical and electrochemical properties of the Sn/Al phase boundary satisfy conditions for the formation of atomic hydrogen and its reaction with Sn. Electrochemical corrosion plays an important role at the stage of formation of atomic hydrogen. The penetration of hydrogen and its accumulation in the bulk of the alloy is due to the high energy of the phase boundary and the low energy of formation of unstable tin hydride.

Keywords Sn–Al alloy · Embrittlement · Phase boundary · Hydrogen

Introduction

Metal–hydrogen systems have aroused considerable interest as reliable, safe, ecological, and economical

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energy-storage systems of the future. The problem of developing new economical methods for the production of hydrogen from water is also of current interest. The present paper continues our earlier study of the embrittlement of the Sn–Al alloy in humid air [1]. This study is important because of the application of Sn–Al alloys for clad layers for sliding bearings in the motor industry, and as catalysts in reactionary systems [2, 3]. In addition, the Sn–Al alloy can be applied for hydrogen storage in the case of the controllable emission of hydrogen. The data available as well as our own mechanical tests demonstrate that the Sn–Al eutectic alloy loses its plasticity after being exposed to humid air [1]. This phenomenon was described in Ref. [4] and was explained by the formation of a brittle surface film due to corrosion processes. However, in Ref. [1] we found that the brittleness has an intercrystalline origin and is connected with the failure of adhesion on Al/Sn phase boundaries. At the same time the phenomenon is accompanied by the emission of hydrogen from the bulk of the Sn–Al alloy. It is known [5] that the role of hydrogen embrittlement in corrosion phenomena is ambiguous and in each case depends on many factors. The proposed earlier [1] mechanism of hydrogen embrittlement did not explain the facts of the irreversible brittleness of Al/Sn phase boundaries and the emission of hydrogen. Many problems, such as chemical and structural properties of the free surface and the interface of the alloy after contact with water vapour and the possible destruction of the Sn/Al phase boundaries by accumulated hydrogen, have remained unsolved.

The aim of this work is to investigate the change of chemical composition, structural and mechanical properties of the Sn–Al alloy and the Al/Sn phase boundaries after contact with water vapour.

Experimental

The eutectic alloy (99.5 wt% Sn–0.5 wt% Al) and bimetallic solid phase joints of tin and aluminium were prepared from 99.999% aluminium and 99.95% tin. Bimetallic joints with atomically clean

interfaces were obtained by a special cold-welding method at room temperature [6] and were used as macromodels of the phase boundary. The secondary-ion mass spectrometry (SIMS) method was used for investigation of the chemical composition and hydrogen distribution [7, 8]. Ar^+ ions with an energy of 6 keV were used, the ion sputtering rate being 1.5 nmmin^{-1} . Chemical composition, fractographic and structural investigations were conducted by use of X-ray diffraction (DRON, Cu K α 1), energy-dispersive X-ray spectrometry (EDAX) techniques (SEM-LEO 435 VP, Roentec EDR-286), optical microscopy (Neophot 30), and scanning electron microscopy (JEM-100, ASID-4D). Standard tensile tests were used for estimation of the mechanical properties of the alloys and the bimetallic joints. Exposure to water vapour was carried out at 293 K in air at 70–100% humidity. The kinetics of the Sn–Al embrittlement was investigated previously [1]. In this work, the duration of exposure to water vapour is given in the figure captions.

Results and discussion

As shown in Fig. 1, the SIMS depth profile analysis of the Sn/Al phase boundary reveals that there was a considerable amount of hydrogen on the boundary. However, besides hydrogen, a slightly increased amount of oxygen compared with that distributed within the bulk was observed near the phase boundary. This suggests that the water-vapour-induced change of the strength of the phase boundaries in the eutectic Sn–Al alloy is caused by the influence of hydrogen and oxygen. Probably, an oxidation process accompanies the penetration of hydrogen along the phase boundaries and leads to an irreversible failure of the phase boundary adhesion. For confirmation of this hypothesis, let us consider the results of the X-ray and SIMS analyses of the Sn–Al alloy. By the way, the X-ray method could detect the presence of grey tin, because as is known, that conversion of white tin (β -Sn) into grey tin (α -Sn) is accompanied by brittle destruction (“tin pest”). This was not observed from the X-ray analysis of the Sn–Al alloy, which showed no α -Sn in the alloy after its long-time exposure to water vapour (Fig. 2). Instead, the weak signal of SnO_2 was seen in the spectra, indicating the presence of oxidized layers of Sn. The X-ray spectra contained no information about aluminium. This was

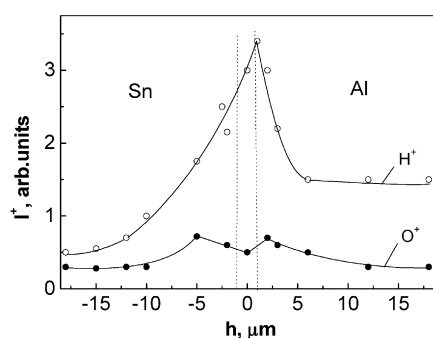


Fig. 1 Depth profiles of the secondary-ion mass spectrometry (SIMS) signal intensity of hydrogen and oxygen on the Sn/Al phase boundary after contact with water vapour for 24 h. Position 0 corresponds to the phase boundary

because of the small amount of aluminium in the alloy. The results of the SIMS analysis of the Sn–Al alloy (Fig. 3) showed that the intensity of the Sn^+ signal increases after exposure to water vapour. The increase of the SIMS signal from metals always accompanies the formation of metal oxides. In our case, the sevenfold increase of the Sn^+ signal is probably related to the formation of the oxidized layers of Sn. As concerns the aluminium phase, it is necessary to take into account the small amount of aluminium in the alloy. For the aluminium content, an intensity I_{Al}^+ of about 0.11 arbitrary units is expected; however, I_{Al}^+ was even higher and reached the value of 6 arbitrary units. This relative magnification was more significant for Al ($I_{\text{Al}}^+ \text{ alloy}/I_{\text{Al}}^+ \text{ pure} = 55$) than for Sn ($I_{\text{Sn}}^+ \text{ alloy}/I_{\text{Sn}}^+ \text{ pure} = 7$), which is in agreement with the intensity of the SIMS signals for oxides of Al and Sn [7]. Regrettably, we cannot detect precisely the structure of the compounds formed on the interphase. Most likely, they could be nonstoichiometric intermetallic oxide compounds.

From Fig. 1 it follows that hydrogen does not merely accumulate on the phase boundary but penetrates also into both metals. The hydrogen penetration depth measured from the phase boundary is larger for tin than for aluminium. This is also confirmed by fractographic investigations, which show that in the long run the hydrogen embrittlement also expands into the grain boundaries of tin (Fig. 4). This provides evidence for the dominating interaction of hydrogen with tin on the interface. The interaction of hydrogen mainly with the tin surface could be explained by the low energy of formation of SnH_4 hydride (252 kJmol^{-1} for AlH; 147 kJmol^{-1}

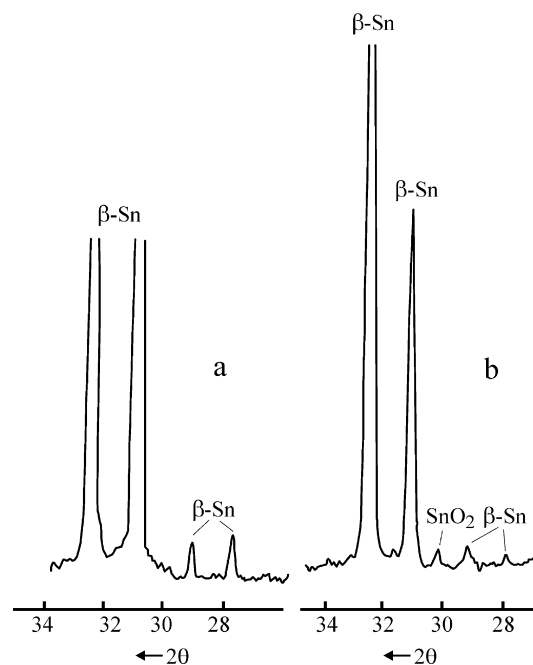


Fig. 2 X-ray diffraction patterns of pure Sn (a) and of the Sn–Al alloy (b) after contact with water vapour for 1 month

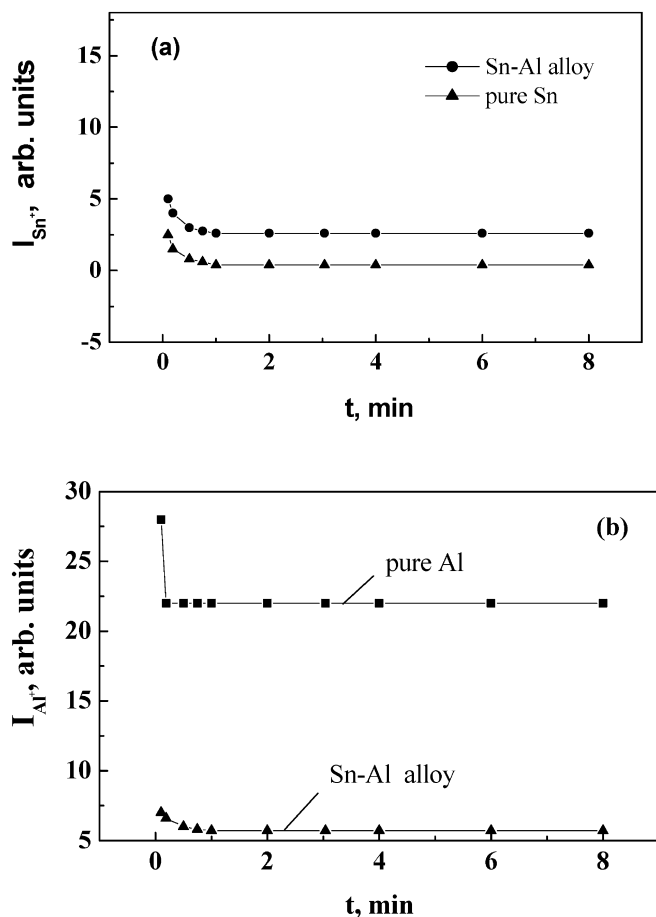


Fig. 3 Depth profiles of **a** the Sn⁺ and **b** the Al⁺ SIMS signal intensity of pure metals and the Sn–Al alloy after contact with water vapour for 1 month

for SnH and -71.4 kJmol^{-1} for SnH₄). However, it is known [4] that the formation of SnH₄ occurs only upon the fulfillment of two conditions: the presence of atomic hydrogen and of free bonds of tin. The specific properties of the Sn/Al phase boundary satisfy these conditions.

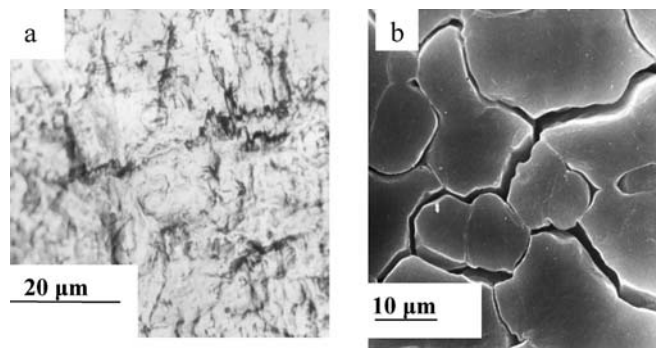


Fig. 4 View of **a** the Sn and **b** the Al surfaces after interfacial fracture of the Sn/Al bimetallic joint exposed to water vapour for 1 month. The grain boundary brittleness of the Sn phase is clearly seen

Let us consider the properties of the Sn/Al phase boundary. In Ref. [1] it was shown that the Sn/Al phase boundary has a higher energy (0.36 Jm^{-2}) than the energy of grain boundary for Sn and Al taken separately. Such relatively high values are due to the large positive energy of mixing (4.2 kJmol^{-1}), which, in turn, indicates low energy of the bonds of Sn with Al. There are always sites of the broken contact and free bonds on the Sn/Al interface. In particular it was confirmed by the microscopic observations, which established the selective character of the development of cracks. The structural investigations by the EDAX technique have shown that the preliminary plastic deformation leads to the formation of many cracks on the Sn/Al phase boundaries (Fig. 5) facilitating the interfacial reactions and embrittlement of phase boundaries during mechanical tests.

The appearance of atomic hydrogen on the Sn/Al interface is caused mainly by electrochemical processes occurring owing to the great difference in the standard electrode potentials (for Al $E_{\text{H}}^0 = -1.66 \text{ V}$, for Sn $E_{\text{H}}^0 = -0.14 \text{ V}$ [4]). In water solution Al is the anode, Sn is the cathode. A peculiarity of this phenomenon is that atomic hydrogen is not converted into molecular form on the surface, but penetrates along phase boundaries into the alloy. The penetration of hydrogen is determined by the low energy of the formation of tin hydride. On the other hand, it is also known that SnH₄ is unstable and decomposes at room temperature [4, 9]. The instability of tin hydride leads to accumulation of hydrogen in the bulk of the alloy and its conversion into the molecular form. The accumulation of molecular hydrogen can create stable cracks or bubbles. Such a phenomenon of hydrogen enrichment at grain boundaries was reported in Refs. [10, 11], where it was shown that as a result of interaction of water vapour with a surface of an Al–Zn–Mg alloy cracks and bubbles are formed on internal grain boundaries. Near-surface cracks open ways for hydrogen to exit, at the same time facilitating the penetration of oxygen. These hydrogen-induced cracks may affect the development of brittleness of the Sn–Al alloy. Let us consider the possibility of the

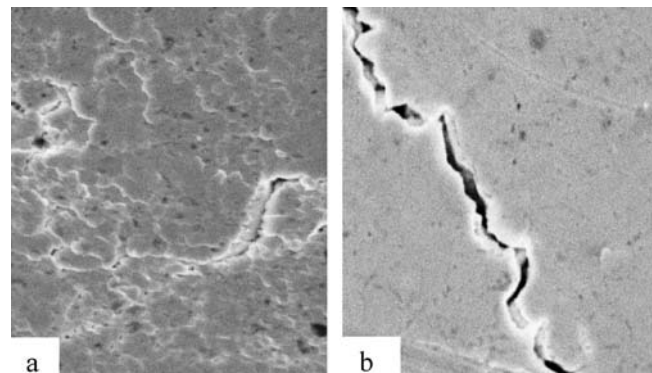


Fig. 5 Energy-dispersive X-ray spectrometry scanning electron microscopy micrograph of the deformed Sn–Al alloy **a** before and **b** after contact with water vapour. Magnification $\times 2,000$

appearance of microscopic critical cracks on the Sn/Al phase boundary according to the Griffith criterion of brittleness: $\sigma = \frac{EW}{\pi c}$, where σ is the tensile stress, W is an adhesion work, c is the crack size and E is Young's modulus. The adhesion work is defined as $W = \gamma_0^{\text{Al}} + \gamma_0^{\text{Sn}} - \gamma_{\text{pb}}$, where γ_0^{Al} and γ_0^{Sn} are the free surface energies of Al and Sn, and γ_{pb} is the Al/Sn phase boundary energy. Assuming that for the Al/Sn phase boundary $\sigma = 45$ MPa [1], $E = 5.104$ MPa, $\gamma_0^{\text{Al}} = 0.7$ Jm⁻², $\gamma_0^{\text{Sn}} = 0.54$ Jm⁻² [4] and $\gamma_{\text{pb}} = 0.36$ Jm⁻² [1], we obtain the critical crack size $c \approx 7$ μm . Microstructural investigations showed that the 5–15- μm cracks appeared on the surface of the alloy in the places where the emission of hydrogen had occurred.

The investigations of the process of hydrogen emission from the alloy showed that within 1 month 1 kg alloy evolves up to 5–7 l hydrogen. The process decelerates gradually in the course of time. However, on the destruction of the samples, a large amount of hydrogen is liberated.

Conclusions

The irreversible intercrystalline brittleness of Sn–Al alloy exposed to water vapour is connected with the accumulation of hydrogen and the formation of cracks

and oxidized layers on the phase boundaries. Specific physical and electrochemical properties of the Sn/Al phase boundary satisfy the conditions for these processes. Interaction with water vapour and the formation of atomic hydrogen are caused by the differences of the electrode potentials between aluminium and tin. The penetration of hydrogen and its accumulation in the bulk of the alloy is possibly because of the low formation energy of tin hydride and the high energy of the Sn/Al phase boundary.

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