

# The embrittlement of Sn-Al eutectic alloy in water vapour

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The present paper is concerned with the study of strength and structural properties of phase boundaries of eutectic alloy becoming brittle after having been exposed to damp air. Interfaces of solid phase joints of tin with aluminium served as simple phase boundary models for this system. It was found (by SIMS technique) that alloy brittleness is caused by chemical absorption of hydrogen on phase boundaries, which leads to the damage of phase adhesion. The chemical absorption of hydrogen increases due to micro-discontinuities present on phase boundaries. Wetting tests and the results on kinetics of embrittlement show that the effect is a nonreversible one and is associated with the formation of hydrides. The mechanism of embrittlement is discussed in terms of the thermodynamic characteristics of the system investigated.

## 1. Introduction

The data available as well as our own mechanical tests demonstrate that Sn-Al eutectic alloy (97.8 wt % Sn-Al) is ductile in the as-deformed state, but after being exposed to moist air tends to become brittle even when fractured at room temperature.

This phenomenon has received little attention to date, and requires further investigation. It has been assumed to be associated with the formation of a brittle film on the surface of the deformed alloy due to interaction with the air [1]. However, we have found that the fracture mode changes from transcrystalline to intercrystalline with prolonged exposure to air which shows that Sn-Al alloy brittleness is due to volume interaction with air and is not a surface effect. This evidence, as well as other results on atmospheric corrosion in other systems [2, 3] allowed us to assume that the effect of embrittlement is connected with the change of phase boundary properties when Sn-Al alloy is exposed to air.

It is the aim of this paper to study chemical composition together with the structural and mechanical properties of phase boundaries of tin with aluminium to detect the causes of this phenomenon. Since there was some difficulty in studying the interfaces inside the alloy, for

boundary macromodels, we used solid phase joints of tin and aluminium [4].

## 2. Experimental details

The eutectic alloy and solid phase joints were prepared from 99.99% aluminium and 99.94% tin. The properties of phase boundaries were studied on solid phase joints of tin with aluminium obtained by cold welding of metals by use of brittle foil. Figs. 1a and b show how these joints were obtained and tested. Aluminium samples (2) were 2 mm thick, except those of tin (4) which were 1 mm; the brittle foils of stainless steel (3) were 0.1 mm thick. The five-layer "sandwich" then underwent a plastic deformation by means of flat punches, the welding area being 3 mm × 30 mm. Fig. 1c presents a diagram of how a brittle foil acts to provide a clean contacting surface. The brittle foil breaks forming an enclosed crack under the influence of the plastic deformation of metals. The edges of the crack move apart and oxides together with other impurities are evacuated from the contact zone. This technique is described in greater detail in [5].

The mechanical properties of solid phase joints were evaluated by the use of a shearing test in air at 293 K in such a way that tension was applied parallel to the phase boundary.

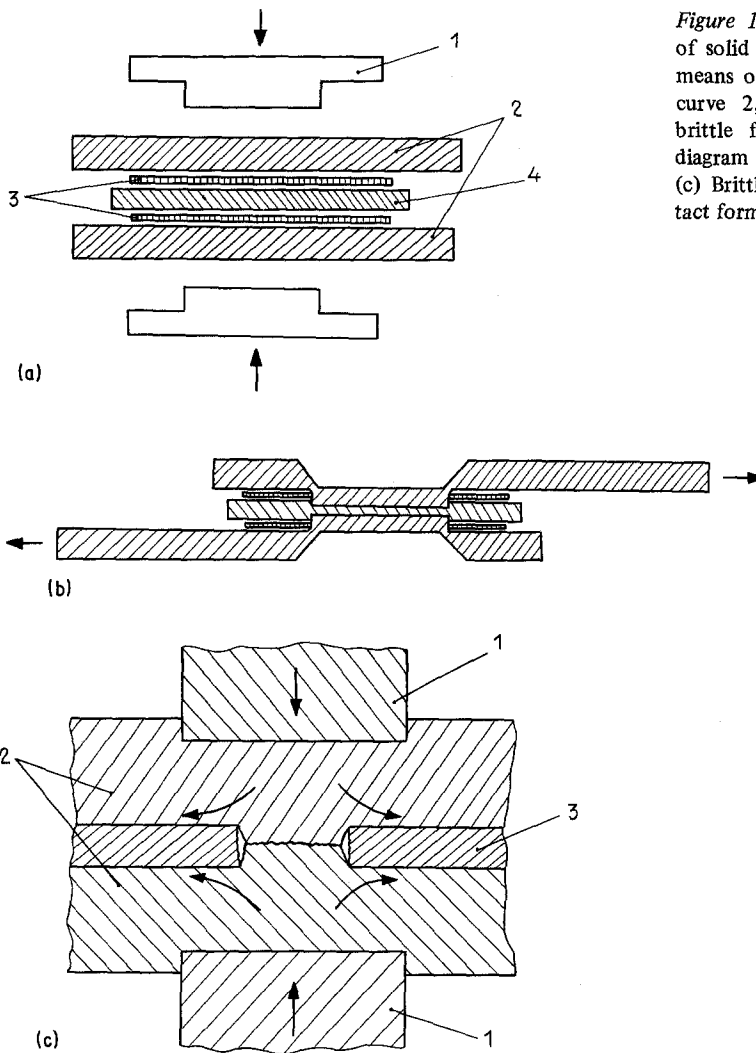


Figure 1 (a) Schematic diagram of obtaining of solid phase joints of tin and aluminium by means of cold welding. Curve 1, flat punches; curve 2, sheet aluminium samples; curve 3, brittle foils; curve 4, tin samples. (b) The diagram of shearing test of solid phase joints. (c) Brittle foil fracture and clean surface contact formation.

The chemical composition of phase boundaries was analysed by SIMS (Secondary Ion Mass Spectroscopy) using sample depth profiling as described in [6]. For this technique  $\text{Ar}^+$  ions with an energy of 6 keV were used, the ion sputtering rate being  $1.5 \mu\text{m min}^{-1}$ . The intensity of the peak of the element investigated served as a working standard. The change of peak was studied during sputtering of joints, starting from the external surface down to the interface and ending with the reverse side of the sample. 2 mm  $\times$  2 mm  $\times$  0.4 mm samples were removed from the welding area and used in a series of experiments. The thickness of samples was satisfactory in terms of a qualitative interpretation.

Both optical and scanning electron (JEM-100, ASID-4D) microscopes were used in structural studies.

### 3. Results

Fig. 2 curve 1 shows the decrease of eutectic Sn-Al alloy strength with the increased exposure to air at 293 K. The scanning micrographs of the fracture surfaces (Fig. 3) demonstrates the fracture morphology of the alloy from a viscous state to that of brittle intercrystalline one.

The results show that a solid phase joint of tin with aluminium displays a sufficiently large shear strength ( $\sim 60 \text{ mNm}^{-2}$ ) and exhibits a ductile fracture mode through the tin phase immediately after manufacture. However, with increased exposure time of the joint to air at 293 K its strength decreased and cohesive fracture of tin changed into a mixed mode involving adhesive failure through the interface of aluminium with tin (Fig. 2, curve 2). After two days, a solid phase joint of tin with aluminium exhibited

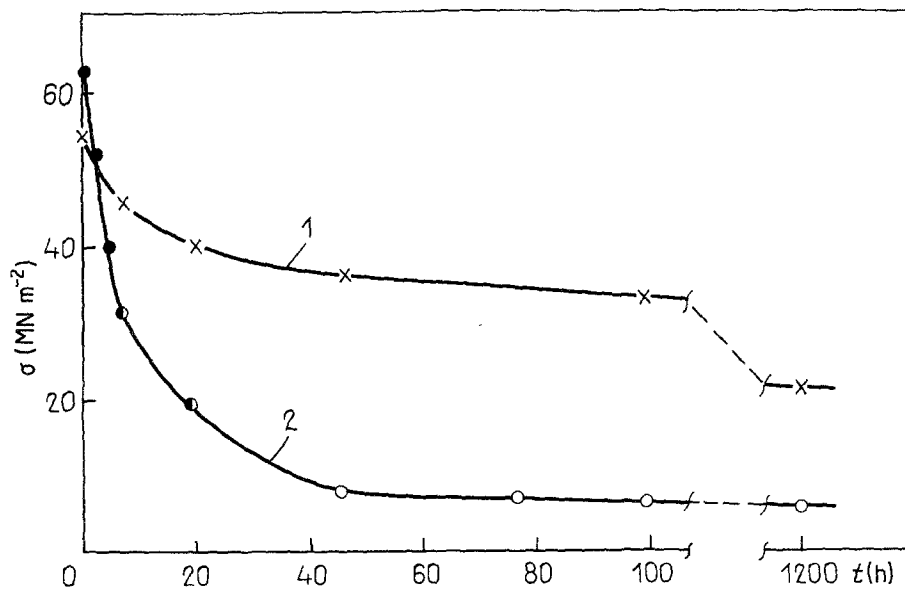


Figure 2 Dependence of strength ( $\sigma$ ) of deformed eutectic alloy (curve 1) and solid phase joint aluminium with tin (curve 2) on exposure time ( $t$ ) in air. ● – fracture on tin, ○ – interface fracture, × – mixed type fracture.

an entirely brittle fracture through the interface. As seen from Fig. 2 embrittlement of a solid phase joint of tin with aluminium is analogous to that observed with the Sn–Al eutectic alloy (curve 1). The difference in kinetics is due to the large area of phase boundaries within the alloy.

Consequently, the embrittlement of Sn–Al eutectic alloy after a long-term exposure to air can be explained by the decrease of phase boundary strength. Experiments on the effect of exposure medium on the strength and type of the fracture showed (Fig. 4) that contact with water intensified (Fig. 4, curve 3) the phase boundary embrittlement, while exposure either to vacuum up to

393 K presented it fully (curve 1). Thus, the decrease of phase boundary adhesion strength in the alloy was found to be due to the interaction of water or of water vapour.

In order to clarify the mechanism of boundary embrittlement by water the chemical composition of the boundary after being exposed to water vapour should be determined.

The SIMS depth profile analysis after a 30 day exposure to water vapour, as shown in Fig. 5, revealed that on the boundary there was not an increased amount of oxygen compared with that distributed within the volume, additionally there were no  $\text{OH}^-$  groups or oxidation products, how-

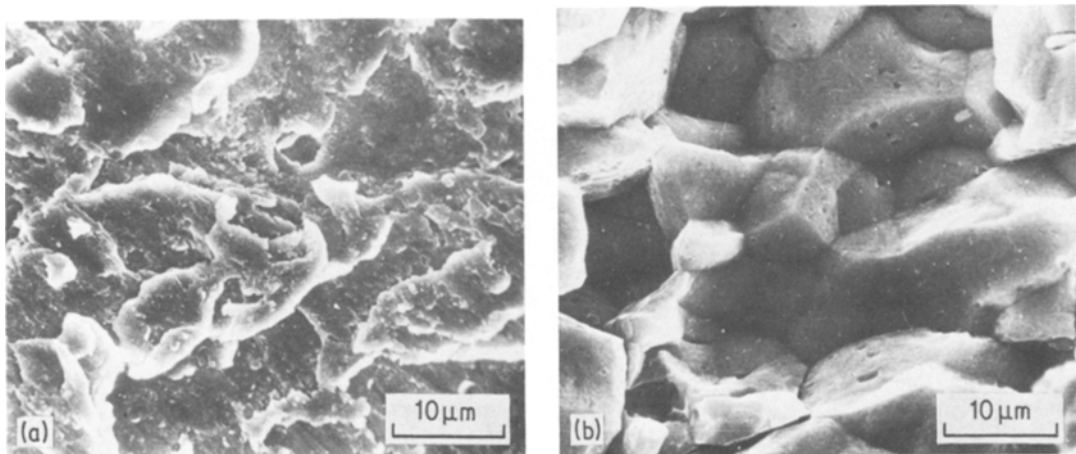


Figure 3 Fracture surfaces of Sn–Al eutectic before exposure (a) and after 1200 h exposure in air (b).

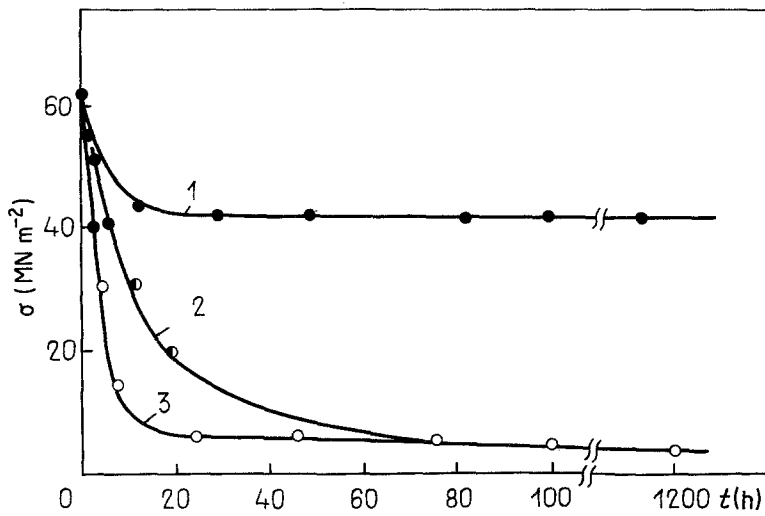


Figure 4 Dependence of solid phase joint strength on exposure time in various media. Curve 1, vacuum, air 393 K; Curve 2, air, 293 K; Curve 3, water.

ever, there was a considerable amount of hydrogen.

This suggests that the change of strength of phase boundaries after eutectic Sn–Al alloy contact with water may be caused by the influence of hydrogen.

It is reported in [2, 3] that the interaction effect of water vapour with the surface of Al–Zn–Mg alloy (studied by means of electron microscopy) with the subsequent transfer of atomic hydrogen to the internal interfaces of alloy. These results confirm the fact that hydrogen appears on phase

boundaries of Sn–Al alloy after having been exposed to atmospheric water.

When considering the curve of hydrogen distribution near the boundary (Fig. 5), other features are apparent, namely, hydrogen does not only accumulate on the boundary but is distributed in both the metals. The distribution depth of hydrogen from the phase boundary is larger for tin than aluminium. This may be relevant to the mechanism of alloy brittleness that must be confirmed by microscopic examination of fracture surfaces.

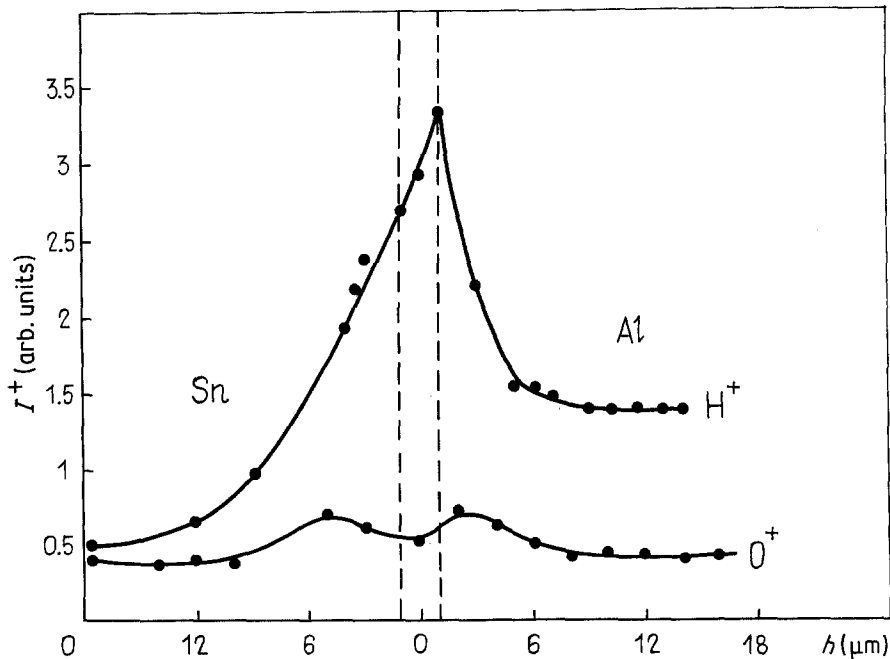
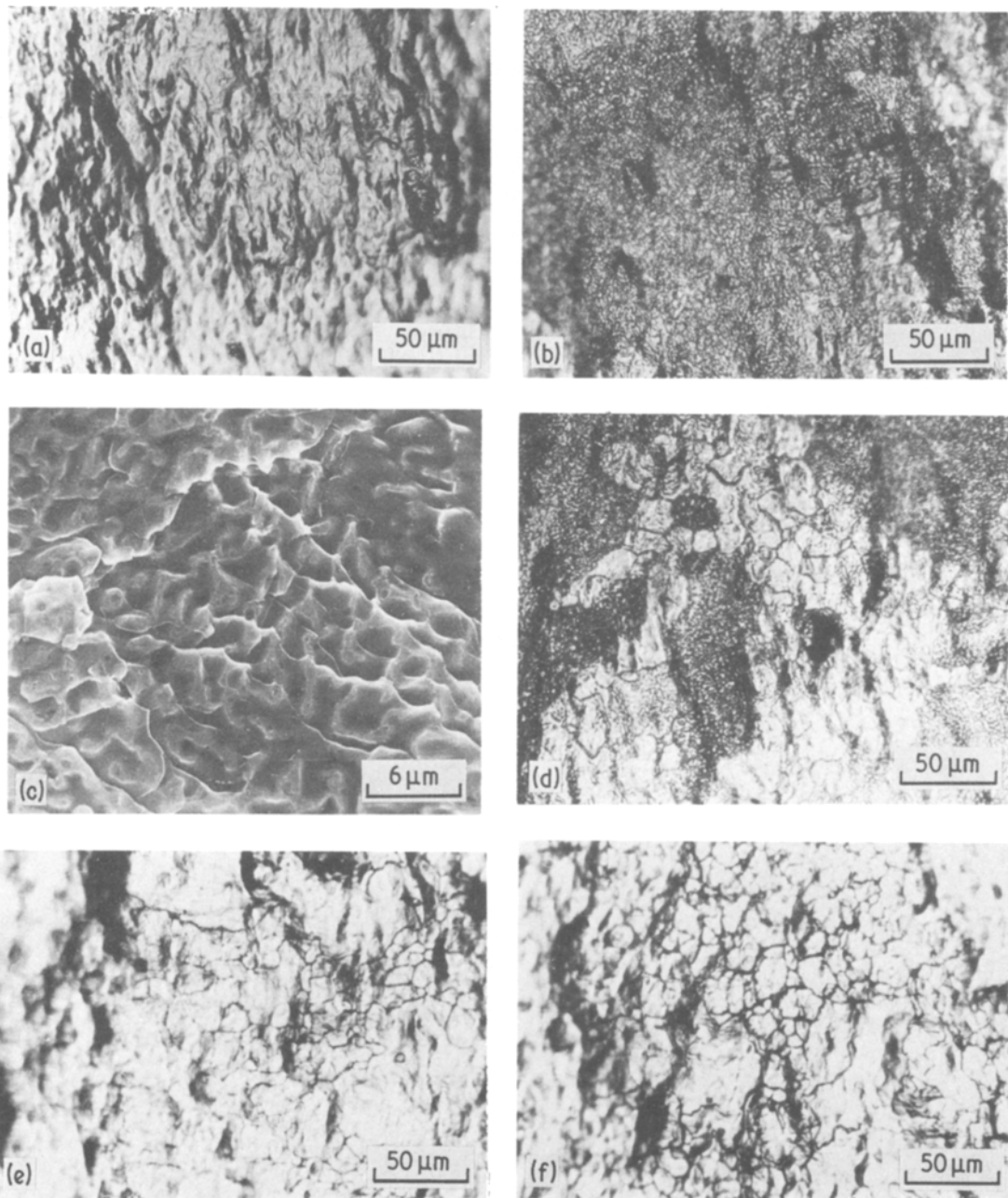


Figure 5 Distribution of hydrogen and oxygen near interface of tin with aluminium.



*Figure 6* Fracture surfaces of solid phase joint during exposure to water vapour after 1 h [(a) aluminium, (b and c) tin], after 5 h [(d) tin], after 24 h [(e) aluminium, (f) tin].

Fig. 6 shows the structure of the contact surfaces of tin and aluminium after 1 h exposure of a solid phase joint to water vapour and subsequent fracture at 293 K. The aluminium surface (Fig. 6a) was bright and smooth, whereas that of tin (Fig. 6b) exhibited surface microrelief. The manifestation of microrelief of tin surface suggests selectivity of the interaction of hydrogen with the

interface. When examining the microrelief of tin surface at higher magnification (Fig. 6c), it can be seen that it is made up of extended regions of tin and areas not exposed to damage during joint fracture. With the increase of exposure time of the joint to water vapour, there appear light and smooth regions free from microrelief on the tin surface (Fig. 6d). After a 24 h exposure to water

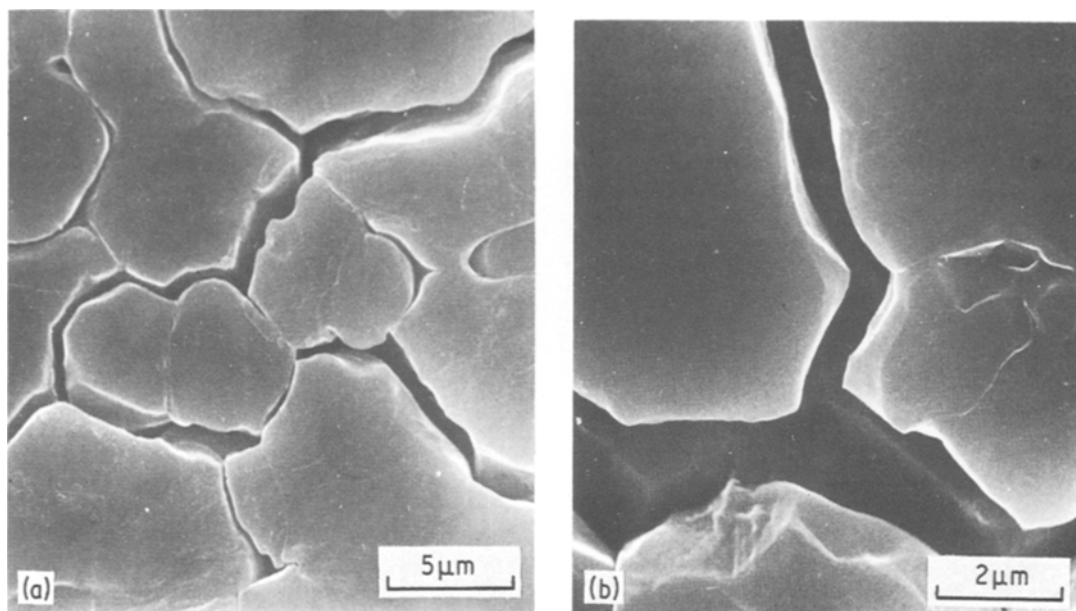


Figure 7 Grain boundary brittleness of tin after 24 h exposure of solid phase joint of tin with aluminium to water vapour.

vapour the tin surface is totally free from microrelief and identical with that of aluminium (Figs. 6e and f). This indicates that the interaction of hydrogen with the entire surface of tin has come to an end. The grain boundaries of tin display significant brittleness. This is also indicated by a structure (Fig. 7) obtained by bending the tin surface. This gives evidence of the dominating interaction of hydrogen with tin on the interface.

Let us now consider the possible causes of low microrelief can arise on the tin surface. On the one hand, this might be due to a nonuniform adhesion in the contact area. The extending regions of tin have likely had an adhesion contact with aluminium during the test, whereas the rest of the tin surface has ceased to be strongly adhered to the aluminium. On the other hand, microrelief of the surface might reflect the process of dissolution of hydrogen in metals. To uncover the nature of surface microrelief, an experiment was set up: a solid phase joint of tin with aluminium after an hour exposure to water vapour was tested by a shock-type force at low temperature. In this case static structure of solution would not change, and, microregions of adhesion contact, on the contrary, would have brittle fracture on the interface. The experimental results were lacking the characteristic microrelief of the tin surface. Clearly, nonuniform adhesion

of contact is thus responsible for the microrelief of tin surface after 1 h exposure to water vapour: beside the regions of tin retaining some adhesion with aluminium there are some where adhesion is absent.

The fact that the process of hydrogen interaction with the interface at the initial stage of embrittlement is selective might be explained by the existence of microdiscontinuity-type structural defects on the interface of aluminium and tin. These defects are likely to be of deformation origin and have probably appeared during manufacturing of the solid phase joint. To find this, we studied kinetics of loss of strength for thermodynamic equilibrium phase boundary of tin and aluminium which is free from any deformation defects.

The above interface was obtained by a long-term annealing of a solid phase joint at 450 K.

In order to measure kinetic dependences of strength decrease of phase boundary, solid phase joints were preliminary annealed and later immersed in water (for different time limits) and finally, underwent a shearing test at room temperature. The investigations show (Fig. 8) that when testing unannealed samples (curve 1) a brittle fracture of interface takes place after 1 h direct contact with water, whereas for annealed samples the contact with water during the same

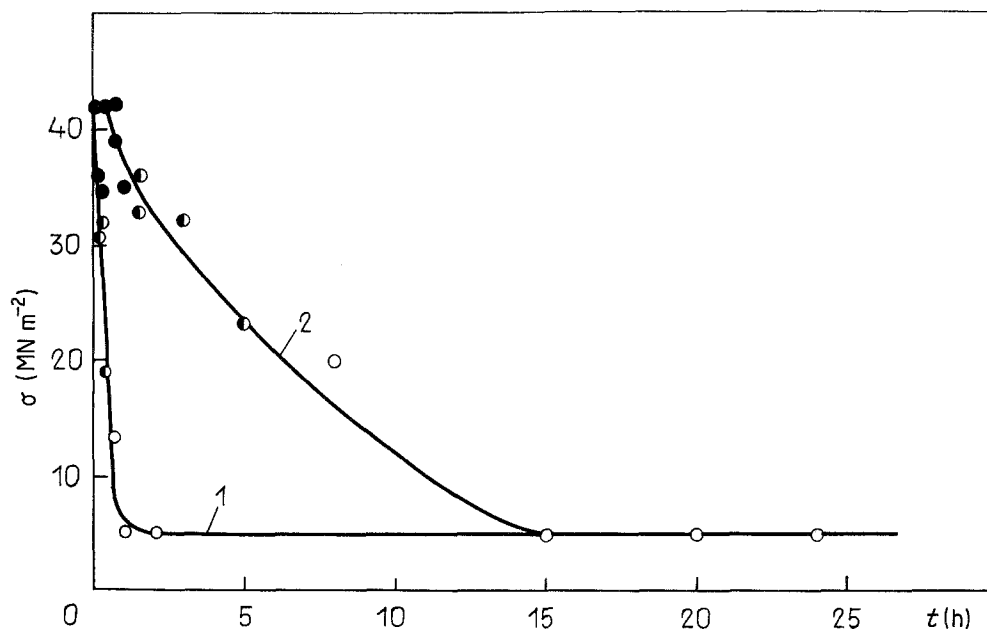


Figure 8 Dependence of strength of solid phase joints of tin with aluminium unannealed (curve 1) and annealed (curve 2) on exposure time to water vapour.

period of time has practically no effect (curve 2). However, a longer time limit of sample contact with water (15 h) leads to unbrittleness. Thus, thermodynamic equilibrium phase boundary is also subjected to hydrogen embrittlement. The role of plastic deformation is that of acceleration of embrittlement.

#### 4. Discussion

The hydrogen embrittlement of metals unfolds in a multitude of ways and has found its reflection in a number of different classifications. For example, reversible and nonreversible hydrogen brittleness are distinguishable. Hydrogen brittleness is considered to be reversible if ductility of metals is fully re-established after hydrogen is removed from the metal, while in the case of nonreversible brittleness there remain defects of hydrogen compounds which decrease the metal strength.

A number of tests were carried out to study reversible brittleness. The first one was as follows: solid phase joints of tin with aluminium were exposed to water vapour for a longer period followed by annealing at 453 K and immediately afterwards underwent a shearing test at room temperature. The results showed that there was analogous brittle fracture of samples along the interface if compared with that before annealing.

Another series of experiments were performed with solid phase samples which were placed in a vacuum chamber at a pressure of  $\sim 10^{-6}$  Pa after having had contact with water. The heating and sample exposure for a longer period in the above chamber did not hinder the process of brittle fracture. These experiments allow to conclude that the hydrogen embrittlement of phase boundary and of the whole Sn–Al alloy was a nonreversible one.

Nonreversibility of hydrogen embrittlement might be caused by a number of effects. Of these, two causes seem to be most applicable to brittle Sn–Al eutectic alloy, and namely, molecular hydrogen in discontinuities and formation of hydrides. In the first case the effect of molecular hydrogen in metal results in stable cracks, which is the main cause of brittleness. The model of crack development under the effect of molecular hydrogen is discussed in [8].

To check the two hypotheses we set up experiments in vacuum to observe aluminium wetting by tin after it has been melted in a solid phase joint. This technique enabled us to avoid the influence of cracks formed by molecular hydrogen. The results reported no aluminium wetting by tin of those samples which were preliminary exposed to water. After the tin solidified, it could be easily removed from the aluminium with

practically no adhesion. The samples which had no contact with water always displayed good aluminium wetting by the tin, and there was significant adhesion after their solidification. Aluminium nonwetting by tin is most likely to occur as a result of relatively stable chemical compounds and hydrides formed on the boundary during hydrogen interaction with metals. The formation of hydrides might turn out to be the main cause of embrittlement both for the phase boundary and Sn–Al alloy.

If hydrides are in a gaseous state, they destroy phase adhesion while their excess pressure leads to alloy fracture along interface. When in a solid state, hydrides have poor adhesion with metals, and this also adds to the formation of crack during phase boundary tests. From the above results obtained by SIMS technique and fractography it follows that hydrogen interacts mainly with tin. This is in good agreement with available data on formation heat of tin and aluminium hydrides ( $252 \text{ kJ mol}^{-1}$  for AlH;  $-71.4 \text{ kJ mol}^{-1}$  for SnH<sub>4</sub> and  $147 \text{ kJ mol}^{-1}$  for SnH [9]). We did not find which tin hydride is formed in Sn–Al alloy, and this requires further investigation. However, this might be a gaseous SnH<sub>4</sub> compound.

It should be noted that for solid phase joints of tin with tin and aluminium with aluminium there is neither brittleness nor hydrogen absorption on the boundaries when they are exposed to air or water vapour. Consequently, the phase boundary of tin with aluminium has specific physical and chemical properties responsible for the formation of atomic hydrogen and its interaction with metals.

To understand the characteristic properties of phase boundary of tin with aluminium, interfacial energy was evaluated in terms of a thermodynamical context. The calculated values of interfacial energy were of the order of  $0.36 \text{ J m}^{-2}$ . The high level of interfacial energy throughout the Sn–Al system is, on one hand, the result of large positive energy of mixing ( $4.2 \text{ kJ mol}^{-1}$ ) which, in turn, indicates a low binding energy of aluminium with tin if compared with those of respective components. On the other hand, large interfacial energies might be due to structure, namely, because of a great number of sublattice defects present on phase boundary, which are caused by different periods of contacting lattices (for aluminium  $a = 0.4 \text{ nm}$ ; for tin  $a = 0.6 \text{ nm}$ ,  $c = 0.38 \text{ nm}$ ).

The two facts, low binding energy and high density of structural defects, might influence the process of hydrogen embrittlement of tin and with the aluminium boundary. The results presented here agree well with those obtained earlier, which concern the strength and fracture mode of solid phase joint of tin and aluminium in terms of temperature and deformation rate functions [5].

## 5. Conclusions

Basing upon the data obtained we can put forward the mechanism of embrittlement of phase boundary of tin with aluminium of the whole Sn–Al eutectic alloy. Atomic hydrogen is formed as a result of water decomposition by aluminium during water contact with Sn–Al alloy. In view of a small diameter ( $0.084 \text{ nm}$ ) atomic hydrogen appears on the phase boundary. It is chemically adsorbed there and tin hydride is formed. This process occurs first in regions of structural microdiscontinuities. The chemical adsorption of hydrogen in these regions leads to a great number of microregions where adhesion contact of tin with aluminium is fractured due to the presence of tin hydride.

Further growth and intermixing of such microregions, which is stimulated by large interfacial energy, maintains intercrystalline brittle fracture during alloy testing.

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