THE EFFECT OF HYDROGEN ON THE DUCTILITY OF ALUMINIUM-TIN ALLOYS

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The effect of hydrogen on the tensile ductility of a series of Al-Sn alloys has been studied by slow strain-rate tensile testing. Only the alloy containing a continuous network of the Sn-phase suffers a reduction in ductility, and this is attributed to increased hydrogen diffusivity. It is shown, however, that the effect is reversible.

INTRODUCTION

It has recently been shown (1) that a solid phase joint of aluminium with tin becomes embrittled on standing in damp air. This system was designed to model the phase boundaries in the tin-aluminium alloy eutectic. The concentration of hydrogen was found by the SIMS technique to be appreciably higher at the grain boundaries than in the bulk, and hence the embrittlement of the boundary was attributed to hydrogen.

A commercially important aluminium-tin alloy (Al – 18wt% Sn – 1% Cu) consists (2) of aluminium grains surrounded by a continuous three-dimensional network of tin along the grain edges and at the grain corners; this structure is termed 'reticular'. This alloy thus contains an abundance of aluminium-tin phase boundaries which may be subject to embrittlement in a damp environment (1). The embrittlement of Al-18% Sn – 1% Cu has thus been the subject of the present investigation. The effect of

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changing the volume fraction of tin has also been studied, hence enabling the degree of continuity of the tin phase and the amount of aluminium-tin interface to be varied.

EXPERIMENTAL METHODS AND MATERIALS

A useful technique for investigating environmental embrittlement is that of slow strain-rate tensile testing. For aluminium alloys, it has been found that a susceptible microstructure, even if testing in an aggressive enviroment, will only suffer environmental embrittlement if strain rates are sufficiently low, i.e. below about 10^{-4} s^{-1} (3). At high strain rates (e.g. 10^{-3} s^{-1}) there is insufficient time for hydrogen to diffuse in sufficient concentration to those sites where brittle decohesion occurs.

Standard tensile test speciens were thus tested at a strain rate of 1.4×10^{-3} s^{-1} (when no embrittlement is expected) and at a strain rate of 2×10^{-6} s^{-1} (when environmental embrittlement is expected to occur in susceptible materials). Tests were conducted in three environments with differing degrees of aggressiveness, namely: dry air (using a packing of anhydrous magnesium perchlorate around the specimen), laboratory air (relative humidity about 60 %) and a salt solution ($NaCl/CrO_4$).

The most dependable parameter to characterize the degree of embrittlemennt is the reduction in area (3), which is not affected by secondary cracking, as are the plastic elongation and the fracture energy.

Four materials have been investigated, and their compositions are shown in Table 1. All four alloys were cast, rolled and then annealed at 350°C for 3 hours. Also given in Table 1 are the grain sizes of the aluminium matrix, expressed as the mean lineal intercept average of measurements in three directions.

TABLE 1 – Compositions and Grain Sizes of the alloys.

Alloy wt %:	Sn	Cu	Fe	Si	Al	Grain Size (μm)
Al18Sn1Cu	17.9	0.99	0.18	0.20	bal.	18
Al10Sn1Cu	10.3	1.01	0.18	0.10	bal.	19
Al6Sn1Cu	6.1	0.98	0.18	0.07	bal	20
Al1Cu	0	0.96	0.16	0.09	bal.	19

In the 18 wt% Sn alloy, the tin forms a continuous three-dimensional network (Fig. 1a,b). The 10 wt% Sn alloy contains particles of tin of reticular form which are interconnected over the length of several aluminium grains, while the 6 wt% Sn alloy has isolated particles of tin. The binary alloy is free of tin.

RESULTS

(i) Tensile Tests of Al18Sn1Cu

The results of tensile tests conducted on Al18Sn1Cu are shown in Table 2. Firstly, it should be noted that for the same environment (laboratory air), decreasing the strain rate from 1.4 x 10^{-3} s^{-1} to 2 x 10^{-6} s^{-1} decreases the percentage reduction in area, i.e. the material becomes less ductile.

TABLE 2 - Tensile Test Results

Test No.	Pre-treatment	Test Environment	Strain rate	% R.A.
1	-	Lab. air	1.4 x 10^{-3} s^{-1}	45.5
2	-	Lab. air	2.0 x 10^{-6} s^{-1}	34.6
3	-	Dry air	2.0 x 10^{-6} s^{-1}	44.1
4	-	Salt sol.	2.0 x 10^{-6} s^{-1}	11.4
5	29 day soak in salt sol.	Dry air	2.0 x 10^{-6} s^{-1}	35.4
6	29 day soak in salt sol + 24 hr anneal at 80°C.	Lab. air	2.0 x 10^{-6} s^{-1}	34.9

On examination by SEM, it was found that the fracture surfaces of the specimen tested at high strain rate was completely covered in ductile dimples (fig. 2a,b). Fig. 2b was obtained using back-scattered electrons, where the tin has a much higher brightness level than the aluminium, due to its higher atomic number. In some regions of these fracture surfaces, exudations of tin may be observed.

Specimen 2, tested in laboratory air at low strain rate, exhibited ductile rupture in the centre of the fracture surface. However, there was a ring round the edge of the specimen which showed an embrittled fracture surface, fig.3. In the embrittled region of this specimen, the aluminium-tin interface appears to have decohered, with the tin particles retaining a similar shape to that in the the undeformed material. Occasionally a tin particle was observed to have broken across a small cross-section. the aluminium grains have undergone some plastic deformation.

On comparing tests at a strain rate of 2×10^{-6} s^{-1} in different environments, it can be seen that the ductility decreases on going from dry air to laboratory air to salt solution. Thus the greater the supply of hydrogen in a testing medium, the greater the reduction in ductility. Attention is drawn to the observation that the ductility of the specimen tested in laboratory air at a strain rate of 1.4×10^{-3} s^{-1} and the specimens tested in dry air at a strain rate of 2×10^{-6} s^{-1} are almost identical. In neither case was there an embrittled region around the edge of the specimen.

Having ascertained that there was an embrittlement effect at low strain rates, which increases with the severity of the environment, tests were performed to see if there was a pre-exposure effect. Specimen 5 was soaked for 29 days in salt solution and then tested in dry air at 2×10^{-6} s^{-1}. The ductility was reduced in comparison with Specimen 3, and a characteristic ring of embrittled fracture surface was identified round the edge of the specimen. It is therefore apparent that the material is susceptible to pre-exposure embrittlement.

Muktepavel and Upit (1) suggested that the embrittlement of their solid phase joint of aluminium and tin was non-reversible. However, when a standard tensile specimen was soaked for 29 days in salt solution and then annealed for 24 hr at 80°C (test 6), there was found to be no effect of the pre-exposure. In fact, on comparing tests 2 and 6, it is seen that they exhibit almost identical ductilities. The embrittlement process is thus seen to be reversible in the present material.

(ii) Tensile Tests as a Function on Tin Content.

The results of tensile tests at high and low strain rates in laboratory air as a function of tin content are shown in Table 3. From these it can be seen that at both strain rates, a decrease in tin content leads to an increase in ductility. On comparing the data from tests at different strain rates, there is seen to be an embrittlement effect only in the Al18Sn1Cu material. When the fracture surfaces were examined , only the Al18Sn1Cu specimens tested at 2×10^{-6} s^{-1} exhibited a pronounced embrittled ring. The major failure mechanism in all tests was by ductile rupture, the dimples being of a similar size in all tests. However, a careful examination of the Al10Sn1Cu and Al6Sn1Cu fracture surfaces from slow strain rate tests showed some evidence of decohesion at aluminium-tin interfaces (fig. 4).

TABLE 3 - Tensile Data as a function of Tin Content

Alloy	% R.A. at $1.4 \times 10^{-3}\ s^{-1}$	% R.A. at $2 \times 10^{-6}\ s^{-1}$
Al18Sn1Cu	45.5	36.4
Al10Sn1Cu	58.5	58.3
Al6Sn1Cu	64.2	64.6
Al1Cu	75.0	76.8

DISCUSSION

This study has confirmed the observations of Muktepavel and Upit (1) that the aluminium-tin interface in subject to hydrogen embrittlement. However, through the techniques of slow strain rate tensile testing and SEM observation of the fracture surfaces allied with changing the tin content of the alloys, several new points have emerged.

From the first four results of Table 2, it is possible to state that embrittlement takes place by the diffusion of hydrogen from external media. Test No.5 shows a pre-exposure embrittlment effect on a specimen subsequently tested in dry air. This is due to the protracted period available for hydrogen to diffuse into the structure. The more aggressive the medium, the greater the degree of embrittlement, due to the increased hydrogen diffusion.

In contradiction to Muktepavel and Upit, the present work shows that the pre-exposure embrittlment effect is reversible. A possible reason why this effect was not observed by the previous workers is that they did not anneal or leave their specimens under vacuum for a sufficient time for the reversible reaction to take place.

Following their observations, Muktepval and Upit went on to speculate about the mechanism of hydrogen embrittlement of the aluminium-tin interface. They discussed two effects - molecular hydrogen in discontinuities and the formation of hydrides.

However, since the effect has been shown to be reversible, the exact micromechanism of hydrogen embrittlement is thrown into doubt. Numerous models of hydrogen embrittlement have been advanced over the years - e.g. local slip band softening, and reduction in electron charge density. It is not possible with the present evidence to say what is the exact mechanism of hydrogen embrittlement.

Reference to Table 3 reveals an increasing ductility of the alloys (at both strain rates) with decreasing tin content. At the higher strain rate, all failures were by ductile rupture. Since the average dimple size does not vary in the alloys, it can be implied that the difference in ductility isdue to differences in the growth of cavities during 'internal necking', and not in their nucleation. The higher the tin content, the lower this interlinking strain will be.

If the data of Table 3 are examined, it will be observed that only the Al18Sn1Cu material suffers embrittlement. This alloy alone contains a continuous network of Al-Sn interfaces. A hypothesis to explain this observation would be that the Al-Sn interface acts as a fast diffusion path for the embrittling species. There is evidence to show that the Al-Sn interface is embrittled in all the tin-containing alloys (fig. 4), but only near the edge of the specimens. Thus the factor which determines the ductility of the alloys is not that the interfaces are different in any of the alloys, or that when the Al-Sn interfaces decohere there is a higher net stress on the aluminium grains in the high Sn alloys. The factor which controls the ductility of these alloys will be the supply of hydrogen to the Al-Sn interfaces.

In order to demonstrate that the four alloys do indeed have differing diffusion characteristics, permeation tests (4) were carried out. Specimens in the form of hollow cylinders (with one end closed off) with internal diameter 5 mm and external diameter 6 mm were put in a chromate solution (pH 3). The environment inside the cylinder was checked by a gas chromatograph, thus enabling one to detect when hydrogen had diffused from the external medium through the walls of the cylindrical specimen into the centre. The results of these tests do support the hypothesis that the factor limiting the ductility is the transport of hydrogen. It was found that the order of the ease of hydrogen diffusion was in the order of the Sn content of the alloys, namely:

$$18\%\ Sn > 10\%\ Sn > 6\%\ Sn > 0\%\ Sn$$

CONCLUSIONS

1. It is confirmed that the Al-Sn interface can suffer environmental embrittlement.

2. The 18% Sn alloy suffers from a pre-exposure embrittlement effect, but this effect is reversible.

3. Only the 18% Sn alloy shows a reduction in ductility at low strain rates (in laboratory air), and this is attributed to the fact that a continuous Al-Sn interface aids the diffusion of hydrogen in the material.

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Fig.1a Al18Sn1Cu showing reticular tin particles.

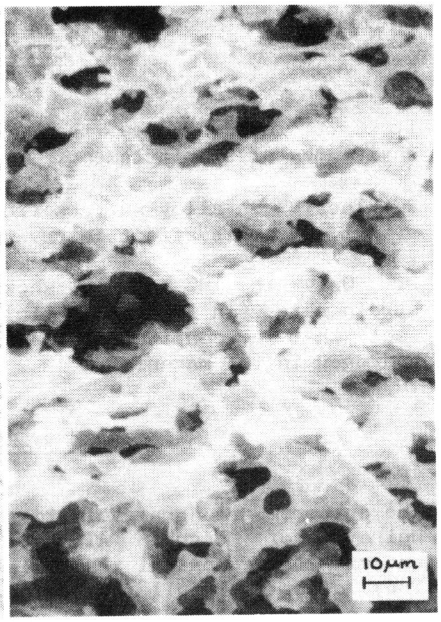

Fig.1b Al18Sn1Cu with Al etched away, showing Sn phase.

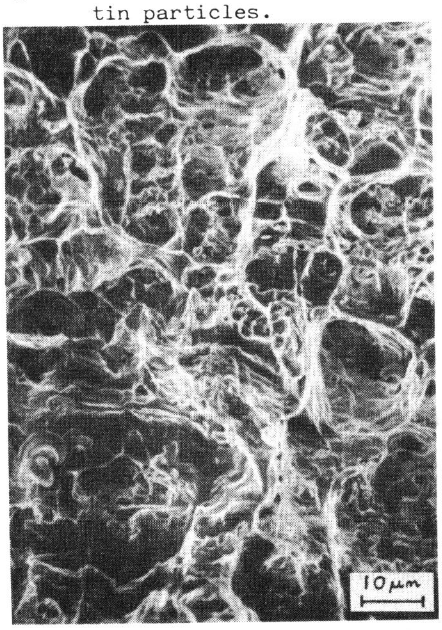

Fig.2a Al18Sn1Cu fracture surface SEI of Testpiece 1.

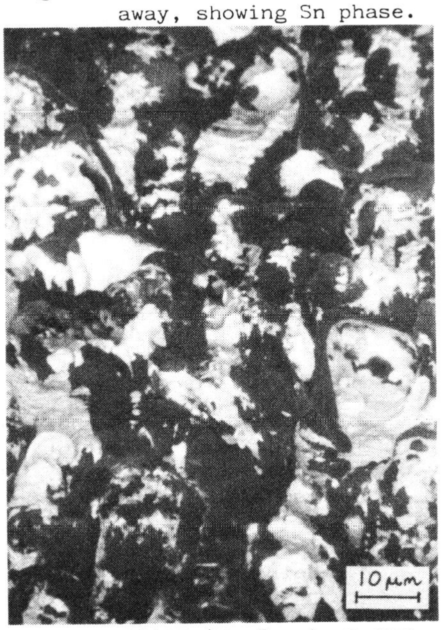

Fig.2b Al18Sn1Cu fracture surface BEI of Testpiece 1.

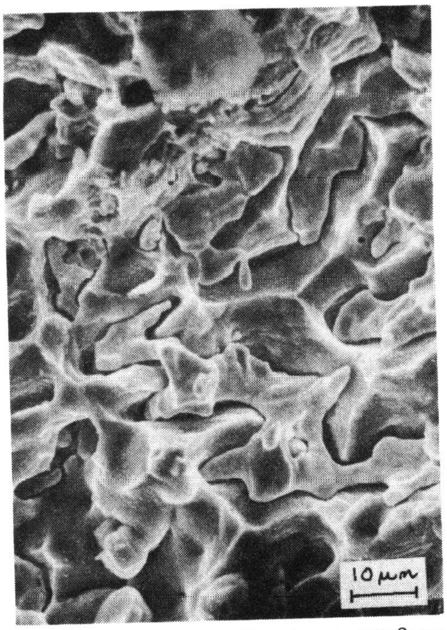

Fig.3 Al18Sn1Cu fracture surface, SEI of Testpiece 2.

Fig.4 Al10Sn1Cu fracture surface SEI near edge.