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Liquid-metal embrittlement of aluminium by several eutectic alloys containing zinc

T. MAE
Department of Metallurgical Engineering, Toyama National College of Technology, Toyama-shi, Toyama-ken, Japan

S. HORI
Faculty of Engineering, Osaka University, Suita-shi, Osaka-fu, Japan

The liquid-metal embrittlement of aluminium plate wetted with Cd–17% Zn, Sn–10% Zn and In–3% Zn eutectic alloy was investigated by tensile tests in the temperature range 423 to 673 K by means of scanning electron microscopy and X-ray energy dispersion. The fracture strain of specimens wetted with Cd–Zn, Sn–Zn, and In–Zn alloys decreased in the temperature ranges 553 to 623, 473 to 553 and 433 to 503 K, respectively, and the specimens were then intergranularly fractured. The minimum fracture strain was largest for the specimen wetted with In–Zn alloy. Intergranular fracture stress decreased with increasing zinc content in eutectic alloys. Zinc was only detected along the grain boundary adjacent to the crack tips. It is, therefore, thought that zinc diffuses into the grain boundary before cracks are initiated by a liquid metal.

1. Introduction

The embrittlement of solid metals by low-melting liquid metals has been studied quite extensively, but the phenomena are not yet fully understood [1, 2]. Liquid gallium embrittlement of aluminium is known as typical liquid-metal embrittlement (LME) [1, 3]. Gallium easily penetrates into the grain boundaries of aluminium [4, 5]. The embrittlement of aluminium wetted with liquid gallium has been studied mainly by performing tensile tests, and it has been observed that the grain-boundary diffusion of gallium is enhanced by loaded stress during the period of the tensile test [6], and also that the gallium content at the grain boundary [7] and the penetration depth of gallium affect the embrittlement of the solid metal [8].

The other element which causes liquid-metal embrittlement of aluminium is zinc. The purpose of the present work was to determine the role of zinc, and if it is similar to that of gallium in the liquid-metal embrittlement of aluminium. Through our experiments [9] we have found out that liquid indium embrittlement of aluminium did not take place in the temperature range less than 903 K, and liquid-tin embrittlement of aluminium occurred in the temperature range higher than 853 K. The eutectic alloys, In–Zn, Sn–Zn and Cd–Zn, were used in this experiment in order to obtain various zinc contents on the surface of the specimen, as well as to obtain liquid-state zinc at relatively low temperature [10].

2. Experimental procedure

Aluminium of 99.99% purity was melted in a high-frequency vacuum furnace and cast into a 80 mm × 80 mm × 100 mm mould. Out of this cast block, 20 mm thick slabs were cut, which then were cold rolled to 90%, to a thickness of 1.0 mm, to obtain specimens for ordinary tensile tests. The guage section of the specimen was 20 mm long and 5 mm wide. The specimens were annealed at 623 K for 7.2×10^3 sec. The average grain diameter of the crystals at this stage was about 80 μm. After annealing the specimens were electrolytically polished in perchloric acid/ethyl alcohol solution (volume ratio 9:1). The eutectic alloys, In–3 wt % Zn, Sn–10 wt % Zn, and Cd–17 wt % Zn, were used in the form of cold-rolled plates of 4 mm × 4 mm × 0.5 mm, which, after washing with trichloroethylene, were spot-welded on to the test specimens.

For the tensile tests, an infrared image furnace was coupled to an Instron-type machine. Tests were conducted in an argon gas stream at a strain rate of $1.67 \times 10^{-3}\,sec^{-1}$. The specimen was heated for 1.2×10^3 sec until the test temperature was reached. In order to ensure temperature stability, the temperature was maintained at the required level for 6×10^2 sec before the test was begun. The apparatus used in the experiment is shown in Fig. 1. The fracture stress and fracture strain are given as engineering stress and engineering strain. The section structure of the fractured specimen was observed by scanning electronic microscopy. For the elemental analysis, the X-ray energy dispersive method was applied.

3. Results

In determining the LME of an aluminium specimen in contact with an attacker alloy, it is most rational to

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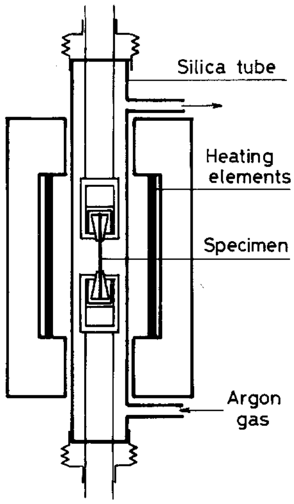

Figure 1 Schematic diagram of the apparatus used in the tensile test of aluminium sheet in contact with liquid alloy.

measure the fracture strain, because in the high temperature range, fracture strain does not necessarily fall even when fracture stress decreases. In the present experiments, therefore, LME was determined according to the fracture strain corresponding to the point where the specimen is fractured, that is, the strain corresponding to the flow stress being zero in the stress–strain curve.

Fig. 2 shows the fracture strain in relation to the temperature. Fracture strain begins to decrease in the range from several degrees up to 20 K beyond the eutectic temperature of the liquid metals (In–Zn 416.5 K, Sn–Zn 471 K, Cd–Zn 539 K), and reaches the lowest point about 40 K beyond the eutectic temperatures. As the temperature continues to rise, fracture strain begins to increase again. The development of strain in each test specimen showed a typical trough which is characteristic for the phenomenon of LME. The strain at the lowest point was the largest for the In–Zn alloy whose zinc content was the smallest of all three alloys.

Fig. 3 shows the relationship between fracture stress and test temperature, as well as the temperature dependence of the ultimate tensile strength of aluminium. The temperature at which the fracture stress of each specimen begins to deviate from the temperature-dependence curve of ultimate tensile strength of aluminium, corresponds to the temperature at which fracture strain begins to decrease, as shown in Fig. 2.

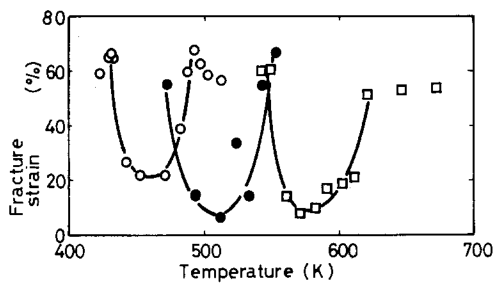

Figure 2 Relationship between fracture strain and the test temperature. A ductility trough is observed for all three alloys. Specimen wetted with (○) In–Zn alloy, (●) Sn–Zn alloy, (□) Cd–Zn alloy.

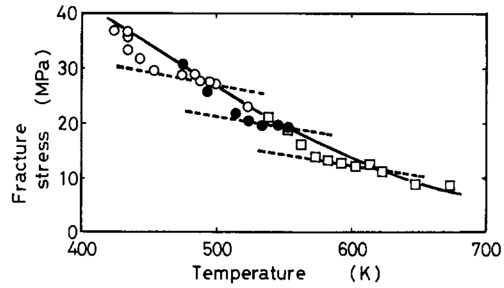

Figure 3 Relationship between fracture stress and test temperature. (——) Ultimate tensile strength of aluminium. Specimen wetted with (○) In–Zn alloy, (●) Sn–Zn alloy, (□) Cd–Zn alloy.

Fracture stress decreases rapidly until the temperature of the lowest fracture strain is reached. Beyond that point, decrease in fracture stress took place only slowly. The temperature at which the tensile strength of the specimen with attacker alloy and of those without the alloy became equal, roughly corresponded with the temperature at which ductility recovered.

The sections of specimens on which tensile tests were conducted were then examined. Figs 4 to 6 show back-scattered electron micrographs of the sections of the specimens with eutectic alloys at the moment of least fracture strain (test temperatures: Cd–Zn 583 K, Sn–Zn 513 K, In–Zn 473 K). In all specimens intergranular fracture occurred, and secondary cracks were observed growing from the fractured section in the longitudinal direction along the grain boundary (parallel to the direction of tensile stress). In the grain boundary adjacent to the tips of the secondary cracks, white contrast image is observed, which indicates the existence of an element heavier than aluminium. X-ray analysis revealed this to be zinc. The results of the analysis are given in Table I. Table I shows clearly, as the zinc content in a eutectic alloy becomes bigger, the further away it lies from the surface of the specimen. In the grain boundary adjacent to the crack tips, only zinc was detected. It was also observed that aluminium was dissolved in the eutectic alloy on the surface of the specimen, as well as within the cracks.

4. Discussion

When zinc is added to metals such as cadmium, tin and indium, which usually do not cause LME of aluminium [11, 12], embrittlement of aluminium occurs in a certain temperature range. As shown in Table I, aluminium is found to be dissolved in the remaining alloy on the fractured surface of the specimen or in the metal around the cracks. Because the zinc content in the liquid metal increases in the direction towards centre of the specimen, starting from the surface, the middle of the cracks and the grain boundary adjacent to the crack tips, it can be assumed that the diffusion of zinc into the grain boundary affects the LME to a large extent. In other words, zinc diffusion, enhanced by the loaded stress during the tensile test, causes cracks, when zinc reaches a certain concentration within the grain boundary at a certain distance from the surface. It was also noticed that the higher the zinc concentration became, the higher was the

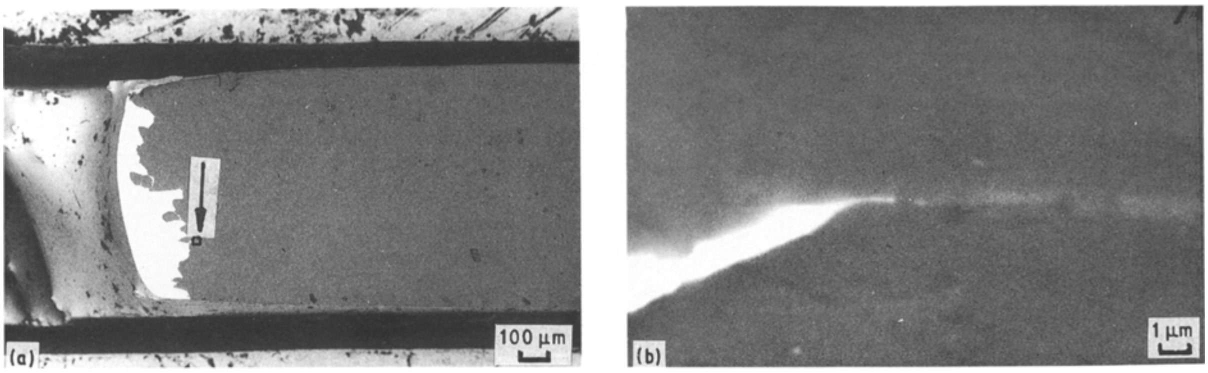

Figure 4 Back-scattered electron micrographs of a longitudinal section of a specimen wetted with Cd–17% Zn alloy. (b) is a magnification of the spot in (a). Tensile test at 583 K.

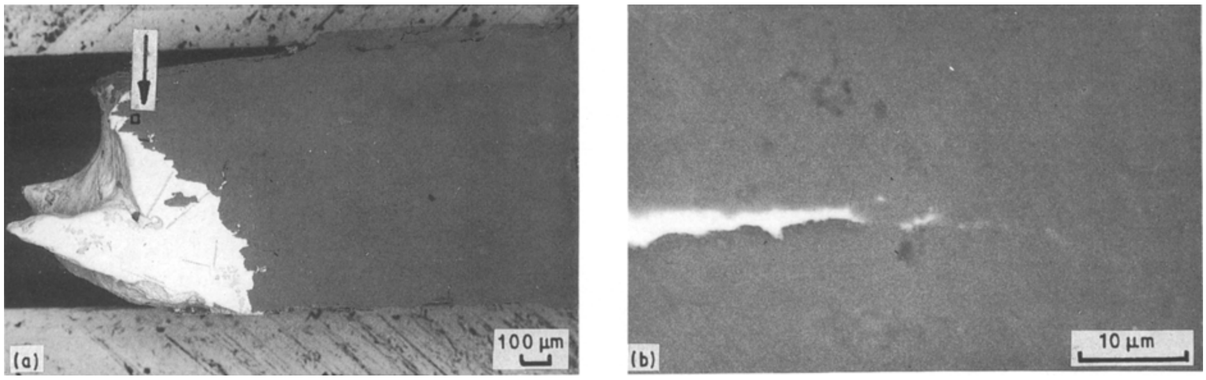

Figure 5 Back-scattered electron micrographs of a longitudinal section of the specimen wetted with Sn–10% Zn alloy. (b) is a magnification of the spot in (a). Tensile test at 513 K.

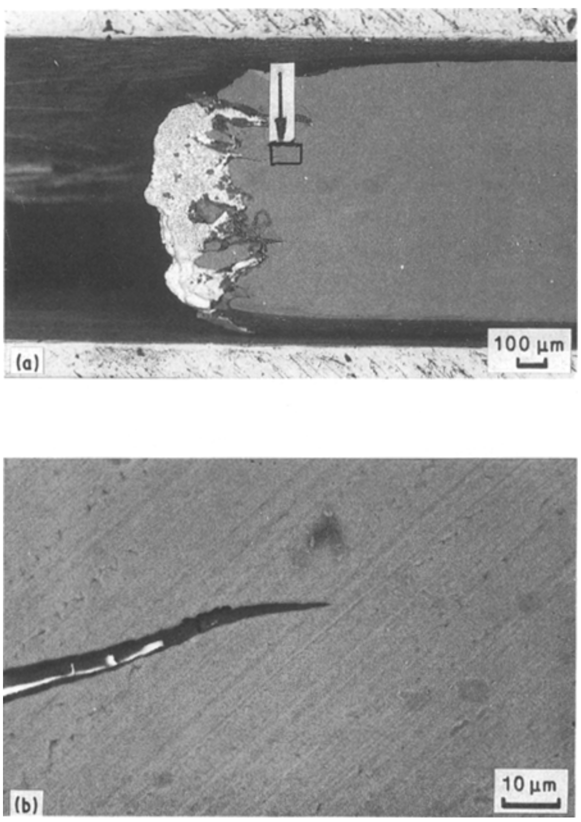

Figure 6 Back-scattered electron micrographs of a longitudinal section of the specimen wetted with Sn–10% Zn alloy. (b) is a magnification of the square in (a). Tensile test at 473 K.

temperature at which the ductility trough appeared. The reason for this is first that the greater the zinc content, the higher is the eutectic temperature, and also the low-temperature point of the trough is defined by the melting point of the liquid metal on the surface of the test specimen. Second, the higher is the zinc concentration, the larger the extent of zinc diffusion along the grain boundary, which reduces the fracture stress of the grain boundary. As a result, there is an increase in the temperature at which the flow stress of aluminium becomes smaller than the grain-boundary fracture stress. Table I shows that zinc concentration in the grain boundary rises as the zinc content of the liquid metal increases. This observation does not agree with the above explanation. To compare the mechanical characteristics of a substance, it is necessary to test them at the same temperature. Because the ductility trough temperature differs among the alloys used, as is the case in this experiment, a direct comparison of the fracture stress depending on zinc content is not possible. Fig. 3 shows that fracture stress begins to decrease rapidly at the temperature where the fracture strain begins to decrease. However, within the temperature range from the point of the least fracture strain to the point where ductility recovers, the temperature dependence of the fracture stress is milder than that of the ultimate tensile strength of aluminium. In addition, the relation between fracture stress and temperature for all three alloys shows a

TABLE I Chemical compositions of alloys on fracture surfaces and secondary cracks, of the grain boundary adjacent to the crack tip in Figs 4 to 6

Eutectic Alloys		Al	Zn (A)	In (B)	Sn (B)	Cd (B)	$\frac{A}{A+B}$
In–3% Zn	FS	0.56	1.01	98.44	–	–	0.01
	SC	1.83	4.15	94.03	–	–	0.04
	GB	99.84	0.36	0.00	–	–	1.00
Sn–10% Zn	FS	7.27	5.14	–	87.59	–	0.06
	SC	58.68	3.04	–	38.28	–	0.08
	GB	96.70	3.30	–	0.00	–	1.00
Cd–17% Zn	FS	0.55	13.50	–	–	85.96	0.14
	SC	5.34	15.52	–	–	79.14	0.16
	GB	93.91	6.09	–	–	0.00	1.00

FS: Fracture Surface, SC: Secondary Crack, GB: Grain Boundary.

parallel tendency. Therefore, it can be assumed that the results in this temperature range indicate a temperature dependence of fracture stress of aluminium caused by zinc. It was observed that the fracture stress falls as the zinc content increases. When the relationship of fracture stress to the zinc concentration was examined, after calculating the fracture stress, σ_f, at the same temperature, e.g. at 473 K by extrapolation, the results given in Fig. 7 were obtained; that is, the fracture stress falls as the zinc-content increases. Based on these results the LME by zinc can be evaluated in the same light as by gallium. Thus, the zinc concentration in the grain boundary increases as the loaded stress increases. However, the more zinc comes into contact with the surface of the specimen, the faster the amount of zinc within the grain boundary increases, and the shorter becomes the time needed to reach the critical concentration, which then leads to fracture. Because the strain rate was held constant in this experiment, the degree of fracture strain also expresses the time needed for fracture to occur. As seen in Fig. 3, the fracture strain of the specimen wetted with In–Zn alloy with the least zinc content is the largest, and the smaller the fracture strain, the more zinc the alloy contains.

From the above explanation it is clear that zinc attached to the surface of the specimen penetrates into the grain boundary under loaded stress and, as the zinc concentration at a certain depth reaches a critical point, cracks occur. Liquid metal penetrates along these cracks, into the inside of the aluminium and causes further cracks, ending finally in fracture.

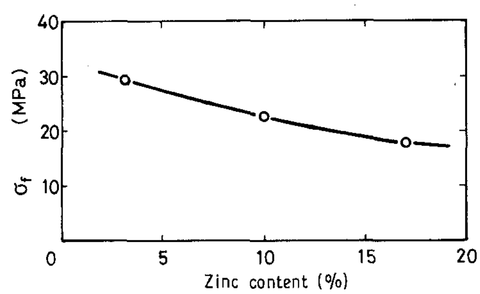

Figure 7 Relationship between fracture stress, σ_f, and the concentration of zinc in eutectic alloys on the surface of a specimen at 473 K. Fracture stress, σ_f is estimated from Fig. 3.

5. Conclusion

A small piece of three different eutectic alloys, Cd–17% Zn, Sn–10% Zn and In–3% Zn, respectively, was spot-welded on to the surface of an aluminium specimen and the influence of zinc concentration in the liquid alloy on the LME of aluminium in the temperature range 423 to 673 K was examined. The following results were found.

1. The fracture strain of the specimens, each wetted with one of the three eutectic alloys mentioned above, fell within a certain temperature range; that is, they showed a ductility trough-effect. The temperature range of the ductility trough lay around 553 to 623 K for Cd–Zn, 473 to 553 K for Sn–Zn, and 433 to 503 K for In–Zn. The temperature where the fracture strain became lowest was 573, 513 and 473 K, respectively.

2. The fracture stress of the specimen at the same temperature, e.g. 473 K, calculated by extrapolation from the temperature-dependence curve of the fracture stress, within the temperature range between the point of lowest fracture strain and the point of ductility recovery, was 19.6 MPa for the Cd–Zn alloy with the highest zinc content, 23.5 MPa for Sn–Zn, and 29.4 MPa for In–Zn alloy with the lowest zinc content.

3. All the specimens with Cd–Zn, Sn–Zn, and In–Zn alloys showed intergranular fracture when the fracture strain was the lowest. From the fractured grain boundary, secondary cracks occurred along the crystal grain boundary.

4. Zinc was detected at the grain boundary adjacent to the secondary cracks growing from the fracture section, as well as in the vicinity of the numerous cracks along the sides of the specimen, whereas virtually no cadmium, tin or indium was detected. These results indicate that zinc diffusion into the grain boundary occurs prior to crack formation.

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