HIGH TEMPERATURE EMBRITTLEMENT OF AN Al-5MASS%Mg ALLOY CAUSED BY IMPURITY HYDROGEN

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Abstract

It was confirmed that an Al-5%Mg alloy showed high temperature embrittlement and an Al-5%Mg-0.04%Y alloy did not. Deuterium was charged to these alloys and tensile tests were performed using a newly developed equipment which enabled us to monitor gas evolution during tensile deformation of test pieces. The Al-Mg binary alloy specimen pre-stretched at the embrittlement temperature evolved hydrogen gases such as HD and D_2 during testing at ambient temperature. On the contrary such gases were not detected during deformation of the Al-Mg-Y ternary alloy specimens. Tritium autoradiography showed that most hydrogen in the ternary alloy was present adjacent to yttrium bearing compounds. This was interpreted that hydrogen in the ternary alloy was trapped by the compounds during pre-stretching and the subsequent deformation. From these results, it was concluded that high temperature embrittlement of the Al-Mg binary alloy was caused by impurity hydrogen.

Introduction

It has been reported that Al-Mg alloys containing magnesium of more than 5mass% show markedly low ductility at temperatures ranging from 200°C to 400°C depending on strain rates (1, 2), and that this ductility trough or high temperature embrittlement (HTE) is based on intergranular fracture resulting from growth and coalescence of cavities at grain boundaries. Itoh and his co-workers have recently reported that the embrittlement almost disappears in the Al-5%Mg alloy prepared by melting and casting in an argon atmosphere, and also in the Al-Mg alloys with a trace addition of Y, Ce, Sm and Be even when prepared in air (3). They have attributed these phenomena to the fact that formation and growth of cavities at the grain boundaries are effectively suppressed so that intergranular fracture is inhibited. They have suggested that high temperature embrittlement in Al-Mg alloys is related to certain gas impurities introduced into the alloys during melting in air, and that the additional trace elements prevent the gas impurity atoms from causing HTE. More recently, it has been suggested that the embrittlement is caused by oxygen atoms dissolved in the matrix or segregated to grain boundaries (4).

However, most of gas impurity atoms dissolved in aluminum alloys is reported to be hydrogen when prepared in air and the solubility of oxygen in solid aluminum is extremely limited (5). Besides, yttrium has a strong affinity for hydrogen (6). Therefore, the role of impurity hydrogen in HTE should be made clear. If hydrogen atoms are closely related to the formation and growth of cavities at grain boundaries, hydrogen molecules may be present in the cavities. In such a case, hydrogen molecules are expected to be evolved from the intergranular fracture surface of the Al-Mg alloy. In order to detect hydrogen evolved from specimens during fracture, a new equipment has been developed by the present authors and has successfully been used in other alloy systems (7, 8). In this paper, HTE was shown to be caused by impurity hydrogen using the newly developed equipment and modified tritium autoradiography was applied to make clear the reason for the inhibition of HTE by the trace addition of yttrium (9, 10).

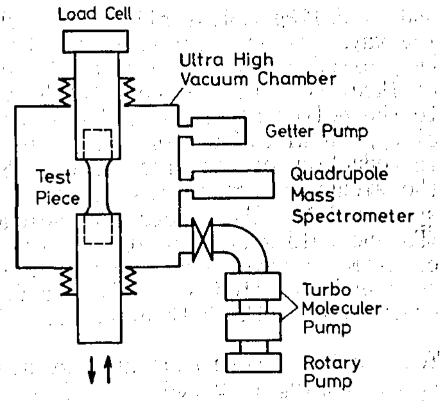

Figure 1. Schematic diagram of an ultra high vacuum testing machine equipped with a quadrupole mass spectrometer.

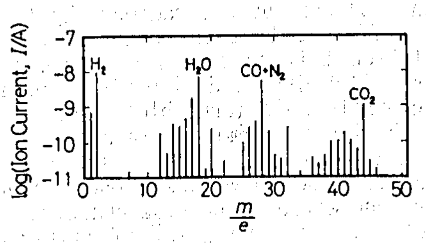

Figure 2. Result of residual gas analysis in the ultra high vacuum chamber of the equipment shown in Fig. 1. Pressure is 2.3×10^{-7}Pa.

Experimental

Newly Developed Equipment for Gas Detection

The developed equipment is shown schematically in Fig. 1 (7, 8). This equipment consists of a tensile compression fatigue testing machine, a quadrupole mass spectrometer, and an ultra high vacuum chamber (the capacity is 50L) which is evacuated with a tandem turbo molecular pump (TMP) and a non-evaporable getter pump (NEG). The pumping speeds of the large TMP, the small TMP and the NEG are 550, 50 and 260$L \cdot s^{-1}$, respectively. The inside of the chamber is kept at a vacuum of about 10^{-7}Pa, and residual gases analyzed under this vacuum is demonstrated in Fig. 2. Hydrogen gas (m/e=2), water vapor (m/e=18), carbon monoxide including nitrogen gas (m/e=28) and carbon dioxide (m/e=44) are mainly remained in the chamber, where m is the mass and e is the valance of the species.

Specimen Preparation and Testing

According to the residual gas analysis (Fig. 2), hydrogen level is still high even in the ultra high vacuum chamber so that it would be difficult to detect a small amount of hydrogen evolved from specimens. On the other hand, evolved hydrogen molecules containing deuterium, i.e., HD (m/e=3) and D_2 (m/e=4) can be detected, since the natural abundance of deuterium is 0.015%. Therefore, Al-5.1mass%Mg ("mass%" will be simply represented as "%" below) and Al-5.1%Mg-0.04%Y alloys were charged with deuterium atoms in the following way. After aluminum of 99.99% purity had been melted in a vacuum of 10^{-3}Pa, mixed gases (argon of 80kPa, oxygen of 20kPa and heavy water (D_2O) vapor of 1kpa) were introduced into the melting chamber. Then, magnesium was added to the molten aluminum, and the resultant alloy was cast. As for the Al-Mg-Y alloy, an Al-3%Y master alloy was added to the molten aluminum prior to the introduction of the mixed gases. Spectroscopic analysis of the ingots showed the amount of impurities of Si, Fe and Cu to be 0.01, 0.004 and 0.001, respectively*. The ingots were homogenized at 430°C for 18h in a vacuum of 10^{-2}Pa and cold-swaged by 70% to 14mm diameter rods. Round tensile test pieces of 10mm in gage length and 10mm in diameter were machined from the swaged rods and annealed at 510°C for 0.5-16h in a vacuum of 10^{-2}Pa so that the grain size of the both pieces was about 0.3mm.

Tensile tests were made at a strain rate of $8.3x10^{-4}s^{-1}$ at elevated temperatures ranging from 200°C to 400°C in a vacuum of 10^{-2}Pa. Tensile tests were also performed using the newly developed equipment at ambient temperature for specimens which were pre-stretched by 26% at 275°C and at the above strain rate. Ten kinds of gas species having different m/e values were analyzed, where the sampling rate was 10msec for each species.

Tritium Autoradiography

Modified tritium autoradiography (9,10), in which the way of tritium charging is different from the other papers (11,12), was carried out to examine the relation between impurity hydrogen and additional yttrium in the following way. Al-5.6%Mg and Al-5.9%Mg-0.06%Y alloys were melted in air and cast into a graphite mold (crucible). To decrease the content of stable hydrogen (^1H) in the ingots (26mm in diameter and 90mm in length), the ingots were remelted in a reservoir at 750°C. The inside of the reservoir was evacuated to 10^{-2}Pa, and the valve was closed before heating. Next, these degassed ingots were subjected to tritium charging: inserted into another reservoir of $170cm^3$ (10) with air and $20mm^3$ of tritiated water (the specific radioactivity was $5.53x10^9Bq \cdot cm^{-3}$), reheated, kept at 750°C for 1h and then water-cooled from the outside of the reservoir.

After the charged ingots were homogenized at 430°C for 18h, specimens of 3x3x3mm were cut from the ingots, free-forged at 200°C into 0.6mm thick sheets and then annealed at 430°C for 0.5-1h. The specimens were mechanically polished, electrolytically polished or etched, covered with collodion layers and finally covered with monolayers of photographic emulsion by the wire-loop method (11) after diluting the raw emulsion (Ilford L-4) by seven times. The covered specimens were inserted into a dark box and kept at -20°C for 0.50-1.38Ms so that the layers were exposed to β-rays emitted from the disintegrating tritium atoms in the specimens. After the exposure, the layers in contact with the specimens were developed by Konicadol-X at 20°C for 300s, fixed by Super Fujifix at 20°C for 600s, rinsed in tap water for 1.8ks, soaked in ethanol, dried and finally subjected to carbon deposition. Observation of the resultant silver particles was made using an SEM (Hitachi, S-

*In relation to the other paper by the present authors entitled " Effect of Sodium on Hot Ductility of an Al-5mass%Mg alloy and an Al-5mass%Mg-0.04mass%Y alloy", content of Na was analyzed to be 0.14massppm using a glow discharge mass spectrometer (VG MicroTrace, VG9000), where the relative sensitivity factor of Na in Al was determined.

2500) equipped with an EDXS device.

Results and Discussion

Hot ductility of the Al-Mg and Al-Mg-Y specimens is shown in Fig. 3. It is confirmed that high temperature embrittlement appears at 275°C in the Al-Mg alloy, and does not in the Al-Mg-Y alloy, as has been reported (3). Fracture surfaces obtained at 275°C are shown in Fig. 4. It is clear that the Al-Mg specimen fractures intergranularly, and that the Al-Mg-Y one, transgranularly.

Before testing using the developed equipment, Al-Mg and Al-Mg-Y specimens were pre-stretched at 275°C up to about 25%. Figure 5 shows a typical result of gas evolution behavior of a pre-stretched Al-Mg specimen during tensile testing at ambient temperature. It can be seen

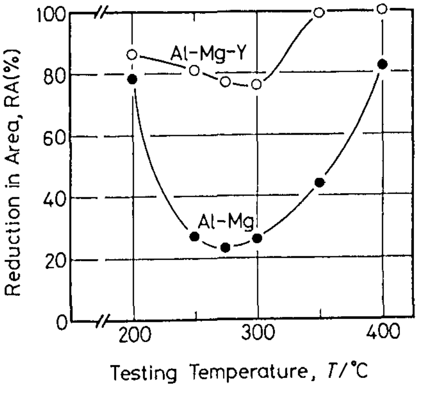

Figure 3. Reduction in area vs. testing temperature curves of Al-5.1%Mg and Al-5.1%Mg-0.04%Y alloys.

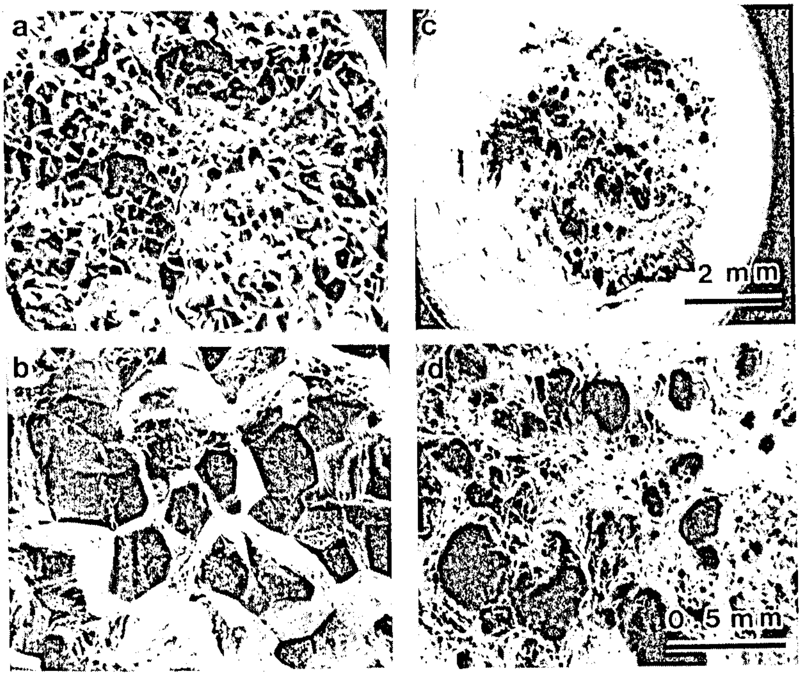

Figure 4. SEM fractographs of Al-Mg (a, b) and Al-Mg-Y (c, d) specimens tested at 275°C.

that hydrogen molecules such as H_2, HD and D_2, methane and argon are evolved during fracture, although evolved H_2 is not clearly detected due to the residual H_2 in the chamber. This figure demonstrates that hydrogen molecules including HD and D_2 are the major gas evolved from the fracture surface. A fracture surface of the Al-Mg specimen used here is shown in Fig. 6. It is noted that the specimen fractures intergranularly as well as that fractures at 275°C (Fig. 4a), indicating that the hydrogen molecules are evolved from the intergranular fracture surface with dimples. The fact that H_2 and HD are evolved means that the alloy contains also hydrogen .rm3" atoms (^1H).

However, it is not clear when hydrogen atoms was introduced into the alloy, since water vapor was present in argon and oxygen gases used dur-

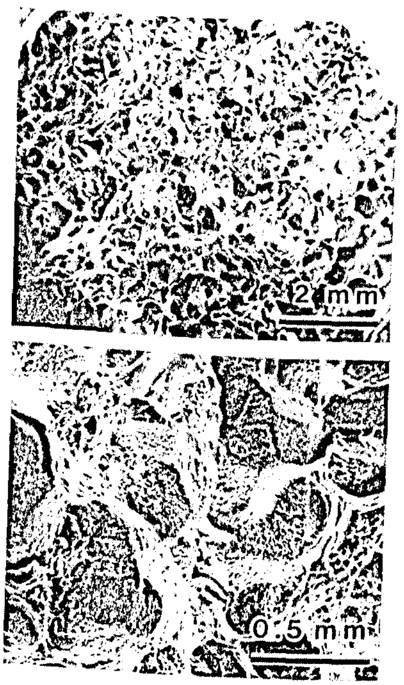

Figure 6. SEM fractographs of an Al-Mg specimen. The specimen was pre-stretched at 275°C and fractured at ambient temperature.

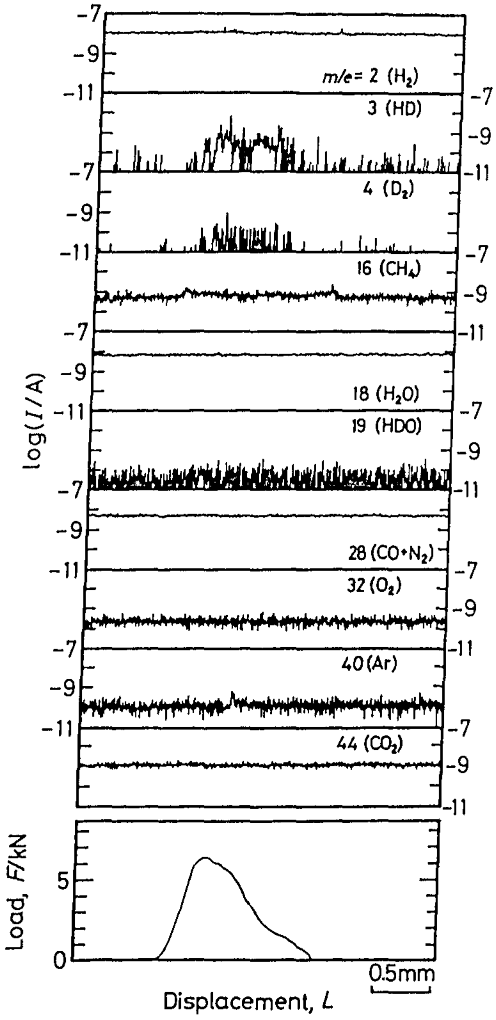

Figure 5. Correlation between a load-displacement curve and gas evolution behavior of an Al-Mg specimen strained in a vacuum of 2.3x10^{-7}Pa at ambient temperature.

ing the melting process, and even present in vacuum, where homogenizing, annealing and pre-stretching were carried out. In a preliminary test, argon was not evolved during fracture of aluminum alloys, when these alloys were prepared by melting in laboratory air and argon was not used for degassing. Therefore, the evolved argon intrudes into the alloy from the melting atmosphere. Methane is considered to be evolved from contaminants on the round surface of the specimen or to be formed through the reaction of hydrogen atoms with carbon atoms on the surface. Argon and methane were evolved also from a commercially available aluminum alloy degassed using argon (7), and the amounts of these gases evolved were about ten times as much as that in the present work.

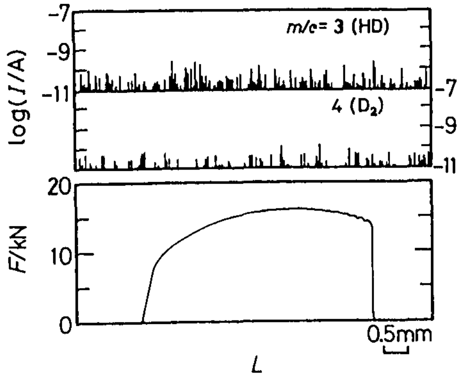

Figure 7. Correlation between a load-displacement curve and gas evolution behavior of an Al-Mg-Y specimen strained in a vacuum of 2.3×10^{-7}Pa at ambient temperature.

Evolution behavior of HD and D_2 was examined also for a pre-stretched Al-Mg-Y specimen(Fig. 7). It can be seen that these gases are not evolved during tensile deformation, although the Al-Mg-Y alloy was charged with deuterium in the same way as in the binary alloy. From the fact that HD and D_2 were evolved only from the fracture surface of the Al-Mg alloy, it is concluded that high temperature embrittlement is caused by impurity hydrogen.

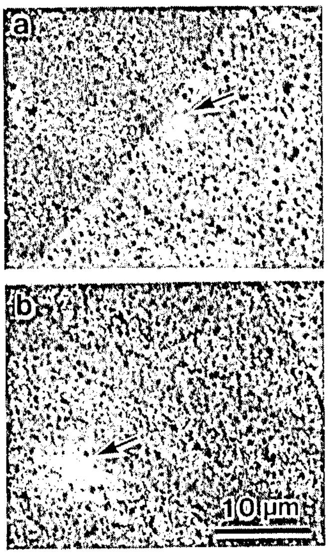

Figure 8. Tritium autoradiographs of an Al-5.6%Mg specimen. Exposure time is 0.5Ms.

Tritium autoradiography was carried out to examine the distribution of hydrogen in the Al-Mg and the Al-Mg-Y alloys. Autoradiographs for the Al-Mg alloy are shown in Fig. 8. Etch pits are seen since the specimen was deeply etched so that the grain boundaries could be visible. The EDXS analysis identified that the arrowed white particles were silver particles, and that the unarrowed white ones are contaminants such as alumina particles introduced during polishing process. Tritium atoms are regarded to be present under the observed silver particles, since the maximum range of the β-ray emitted from a tritium atom is as small as 2.7 μm in aluminum (13) and the resolution (0.9 μm) is about the same dimension as the average diameter of the silver particles (1 μm). It is noted that hydrogen atoms are adjacent to the grain boundaries (Fig. 8a) and are present inside a grain (Fig. 8b). Silver particles were not observed at the grain boundaries on wider autoradiographs. It is thought that hydrogen atoms in the Al-Mg alloys diffuse to grain boundaries during deformation at high temperatures, and that they enhance the formation and growth of cavities at grain boundaries. It would be necessary to investigate the distribution of hydrogen in the alloy strained at high temperatures, while such experiments are considered to be very difficult to undertake on account of limited use of tritium.

Autoradiographs for the Al-Mg-Y alloy are shown in Fig 9. Figures 9A-C are magnified images of the regions designated by "A-C" in the left-hand photo, respectively. The small white particles, some of which are indicated by "Y," are yttrium-bearing compounds, and the large white ones indicated by the arrows are silver particles. Yttrium was present as yttrium-bearing compounds in the ingot, and the compounds were broken into many parts during free-forging. The broken parts have been aligned in the working direction. From these autoradiographs, it can be seen that hydrogen atoms in the Al-Mg-Y alloy are adjacent to yttrium-bearing compounds: presumably hydrogen atoms are present within the compounds or at the interfaces between the compounds and the matrix. Thus, it can be concluded that hydrogen atoms in the Al-Mg-Y alloy are trapped by yttrium-bearing compounds also during pre-stretching at 275°C and that formation and growth of cavities at grain boundaries are inhibited.

Figure 9. Tritium autoradiographs of an Al-5.9%Mg-0.06%Y specimen. Exposure time is 1.33Ms.

Summary

It has been revealed using a newly developed equipment that hydrogen molecules including HD and D_2 are evolved from the intergranular fracture surface of the Al-Mg alloy. On the contrary, such hydrogen molecules are hardly detected from the fracture surface of the Al-Mg-Y alloy, which does not show the high temperature embrittlement. Modified tritium autoradiography, where alloys are charged with tritium during melting, has revealed that hydrogen atoms are trapped by yttrium-bearing compounds in the Al-Mg-Y alloy. The fact that hydrogen is not evolved from the fracture surface of the pre-stretched Al-Mg-Y specimen indicates that hydrogen atoms in this alloy are trapped also during deformation at high temperatures, so that the formation of cavities at grain boundaries inhibited. Thus, it is concluded that the high temperature embrittlement in the Al-Mg alloy accompanied by intergranular fracture is caused by impurity hydrogen.

Acknowledgments

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