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Hydrogen Evolution during Fatigue Deformation in 6061 and 7075 Aluminum Alloys

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Hydrogen evolution behavior during fatigue deformation and fracture in 6061 and 7075 aluminum alloys was examined by using a testing machine equipped with a quadrupole mass spectrometer in an ultrahigh vacuum chamber (QMS-UHV) and by a hydrogen microprint technique (HMT). The QMS-UHV testing revealed that hydrogen was highly evolved at the first cycle in the plastic fatigue. This assumed that hydrogen atoms primarily dissolved were transported to the surface during deformation. It was also revealed that hydrogen evolution behavior in the early stage of plastic fatigue corresponded well with the variation of the applied stress. The amount of hydrogen evolution then decreased according to the number of fatigue cycles. The amount of hydrogen evolved at the fatigue fracture was different from the alloy types; the hydrogen evolution of 7075 alloys was much higher than that of 6061 alloys. The HMT after the fatigue test also revealed that silver particles, which represented the emission sites of hydrogen, were observed mainly around the second phase inclusions.

Keywords: *Hydrogen, Fatigue, Deformation, Mass spectrometry, Hydrogen microprint*

1. Introduction

Aluminum alloys have been regarded as one of the candidate materials for a high compressed (~35MPa) hydrogen tank in the fuel cell vehicles [1,2], since the aluminum alloys show high resistance to hydrogen embrittlement rather than the steels. Among the industrial aluminum alloys, Al-Mg-Si (6000 series) and Al-Zg-Mg (7000 series) ones are believed to be the promising materials for the tank liner. However, the 6000 and 7000 series aluminum alloys are reported to exhibit environmental embrittlement when tested at slow strain rates in laboratory air [3–9] in recent years. This phenomenon is believed to be a kind of hydrogen embrittlement (HE) caused by atmospheric hydrogen. Considering the direction for use of the aluminum alloys as a high compressed hydrogen gas container, it will be important to clarify the fatigue properties of aluminum alloys affected by atmospheric hydrogen to guarantee the safety of the tank. In this study, from a basic point of view, fatigue test was performed by using a testing machine which is equipped with a quadrupole mass spectrometer installed in an ultrahigh vacuum (QMS-UHV) chamber [10,11], together with a hydrogen microprint technique (HMT) [12] to visualize the hydrogen evolution behavior of 6061 and 7075 aluminum alloys.

2. Experimental

2.1 Materials

The materials used in the present study were 6061 and 7075 aluminum alloys; its chemical composition is shown in Table 1. Plate test specimens for the fatigue test with a gage length of 10 mm, width of 5 mm, fillet radius of 1 mm, and thickness of 1.0 mm were cut from a rolled sheet (Smooth). Double U-notched test pieces having a depth of 0.5 mm, a diameter of the notch root of 0.27 mm were also machined on the basis of the dimension of Smooth specimen to fix the fracture zone (Notch). The 6061 alloy specimens were solution treated at 530 ˚C for 20 min and quenched in

water, and then aged at 160 ˚C for 18 h (T6-temper). The 7075 alloy specimens were solution treated at 493 ˚C for 20 min and quenched in water, and then aged at 120 ˚C for 24 h (T6-temper). In all the test specimens, both surfaces were polished by emery papers (#800 and #1200) and buffed with alumina pastes to obtain a mirror-finished surface. The fatigue test to determine the relation between the stress and the number of failure was conducted by using the double U-notched test pieces at the frequency of 1.0 Hz and the stress ratio of 0.1 with the constant stress amplitude with a relative humidity of 50% (RH50%) or 90 % (RH90%). The amount of hydrogen gas contained in the specimens was measured by thermal deposition analysis (TDA) using gas chromatography. For TDA, a highly pure argon carrier gas (99.999 % purity) was passed through a quartz glass tube that contained the test specimen at a flow rate of 20 mL / min. The amount of hydrogen gas was measured at 1 min intervals while the specimen was heated to 600 ˚C. The specimen weighed about 0.45 g and the heating rate was 100 °C / h.

2.2 Hydrogen desorption analysis in the fatigue test

Prior to the test, the specimen was placed on the jig of the tensile testing apparatus equipped with a QMS installed in the UHV chamber. The fatigue test of the specimens was carried out 24 h after maintaining the specimens in a UHV atmosphere in order to obtain a vacuum level of 7.0×10^{-7} Pa. In this study, the baking operation for the UHV chamber was not performed in order to carry out the fatigue test under the constant ambient temperature. The hydrogen evolution from the specimen was evaluated from the hydrogen ion current, where the mass number M/e=2 was selected. The QMS-UHV fatigue test was carried out at the frequency of 1.0 Hz or 0.1 Hz and the stress ratio of 0.1 with the constant stress amplitude. The applied maximum stresses were selected to become slightly higher than the yield stress of 6061 or 7075 alloy specimens.

Table 1 Chemical compositions of 6061 and 7075 aluminum alloys (mass%)

Alloy	Si	Fe	Cu	Mn	Mg	Cr	Zn	Ti	Al
6061	0.56	0.26	0.33	<0.01	1.0	0.17	0.01	0.02	Bal.
7075	0.15	0.28	1.6	<0.01	2.6	0.21	5.5	0.02	Bal.

2.3 HMT

In the HMT, before the testing, the mirror-finished surface was covered with a collodion layer to prevent the reduction of Ag^+ to Ag by aluminum atoms. The collodion layer was then covered with a liquid nuclear emulsion (Ilford L-4, diluted with pure water) containing gelatin and silver bromide (AgBr) crystals using a wire loop method and dried for 15 min. The specimens were fatigue-deformed in laboratory air. The fatigue tests with the HMT were performed in the same testing conditions as the QMS-UHV testing, except for the testing atmosphere of air. After the fracture, the specimens were removed from the testing machine and dipped into formalin (37 mass% HCHO water solution) after the tensile test for 3 s to harden the gelatin layer; then, the specimens were immersed in a fixing solution (15 mass% $Na_2S_2O_3$ water solution) for 8 min to remove the remaining silver bromide particles that did not react with the hydrogen atoms. The arrangement of the silver particles was observed using a scanning electron microscope (SEM) equipped with an energy dispersive X-ray spectrometer (EDXS).

3. Results and discussion

3.1 S-N curves

Figures 1 shows the relation between the stress and the number of cycles in 6061 and 7075 alloys (Notch), respectively. In both alloys, no clear differences of the fatigue properties were observed by changing the relative humidity of the air atmosphere in the present testing condition.

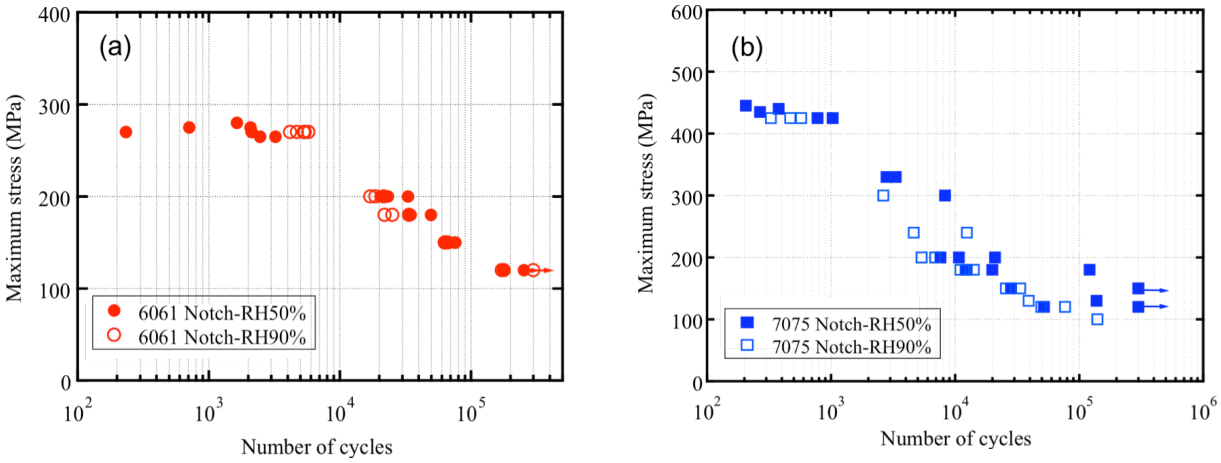

Fig.1 S-N curves of 6061 and 7075 alloys (Notch, frequency: 1.0 Hz, stress ratio: 0.1)

3.2 Hydrogen evolution in the fatigue test

Figure 2 shows the hydrogen evolution behavior in the early stage of the fatigue test of 6061 and 7075 aluminum alloys (Smooth), in which the testing frequency was 1.0 Hz. It was revealed that hydrogen was highly evolved in the first cycle of the loading in both alloys. Hydrogen evolution appeared when the specimens were loaded from the mean stress to the maximum stress, continuously. The magnitude of the first evolution peaks was similar in both alloys ($6\sim7\times10^{-8}$ A). The hydrogen evolution then decreased when the number of fatigue cycles increased. As the number of fatigue cycles increased, the hydrogen evolution peaks relating to the stress amplitude were disappeared. This suggests that hydrogen evolutions, which are associated with stress variation, will appear only in the early stage of the fatigue deformation. It is probable that the hydrogen evolution at the first loading would be related to (1) fracture of oxide films on the specimen surface, (2) stress-induced hydrogen diffusion around inclusions on the surfaces [13] and (3) transportation of hydrogen atoms with the aid of mobile dislocations [14].

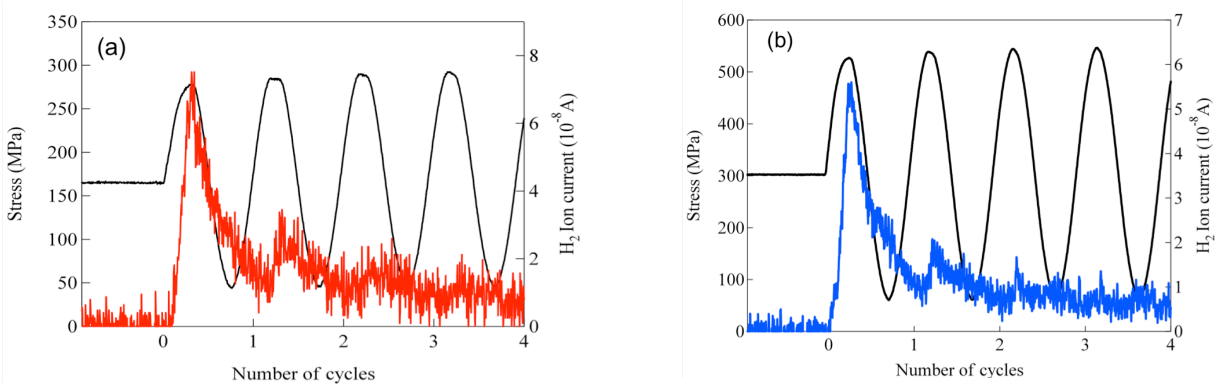

Fig.2 Hydrogen evolution behavior in the fatigue with a test frequency of 1.0Hz, (a) 6061(Smooth), (b) 7075(Smooth).

Figure 3 shows the hydrogen evolution in the early stage of the fatigue test of 6061 and 7075 alloys (Notch), in which the testing frequency was 1.0 Hz. In this case too, hydrogen evolution

peaks corresponding to the variation of stress amplitude were identified. Similarly to the case of Smooth specimens, there was no clear difference of hydrogen evolution in both 6061 and 7075 specimens (Notch). However, when comparing the magnitude of the first hydrogen evolution peaks between Notch and Smooth specimens as shown in Figs.2 and 3, Notch specimens evolved lower amount of hydrogen (3×10^{-8} A) than Smooth specimens ($6\sim7\times10^{-8}$ A). This result implies that the degree of the first hydrogen evolution peaks might be variable according to the magnitude of the stress level in the deformed region.

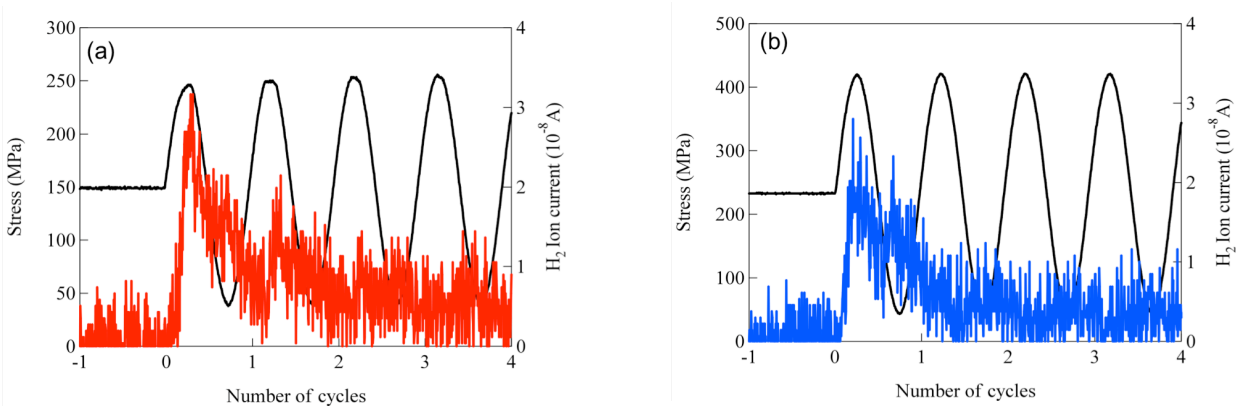

Fig.3 Hydrogen evolution behavior in the fatigue with a test frequency of 1.0 Hz, (a) 6061(Notch), (b) 7075(Notch).

Figure 4 shows the hydrogen evolution in the latter stage of the fatigue test near the fracture in 6061 and 7075 alloys (Notch). In both alloys, hydrogen was highly evolved at the moment of fatigue fracture. The amount of the hydrogen evolution in 7075 alloy was much higher that in 6061 alloy. This hydrogen evolution would be caused by the generation of the fracture surfaces. Since there was no difference of the hydrogen content between 6061 and 7075 alloy before testing on the basis of TDA (12massppm), it is assumed that hydrogen was highly trapped in the microstructure of 7075 alloy, rather than 6061 alloy, just before the fatigue fracture occurred. It is also important to note that hydrogen evolution corresponding to the variation of the stress amplitude was not identified within the four cycles before the fatigue fracture.

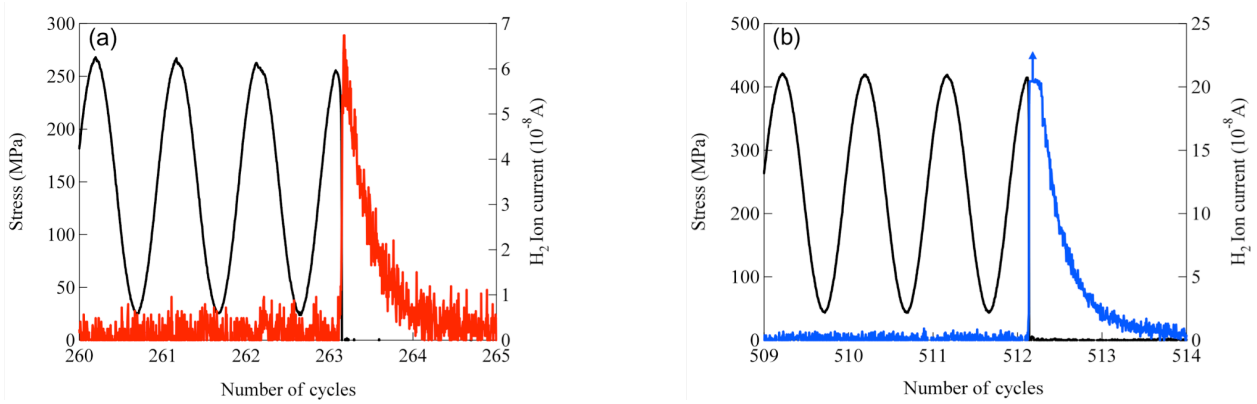

Fig.4 Hydrogen evolution behavior in the fatigue fracture with a test frequency of 1.0 Hz, (a) 6061(Notch), (b) 7075(Notch).

Figure 5 shows the hydrogen evolution behavior in the early stage of the fatigue test of 6061 and 7075 aluminum alloys (Smooth), in which the testing frequency was 0.1 Hz. When the test frequency was 0.1 Hz, a single peak of hydrogen evolution was observed only in the first loading. When the amount of hydrogen evolution is compared between 6061 and 7075 alloys, 7075 alloy evolved higher amounts of hydrogen rather than 6061 alloy. In addition, when the effect of test frequency on hydrogen evolution was compared between 0.1 Hz and 1.0 Hz in Figs.2 and 5, it is found that higher amounts of hydrogen were evolved when the frequency was low (0.1 Hz) in 7075 alloy. This suggests that the hydrogen evolution amounts depend on the strain rate. If the mean strain rates are calculated in the present fatigue condition, 0.1 Hz of frequency corresponds to the 6.8×10^{-3} s^{-1} in 6061 alloy and 8.4×10^{-3} s^{-1} in 7075 alloy. It is also interesting to note that the peak of the maximum hydrogen evolution is not the same timing as the maximum loading. It is assumed that the difference of the mismatch of the timing of peaks between the hydrogen evolution and stress would also represents the change of the hydrogen evolution because of the dependence on the strain rate.

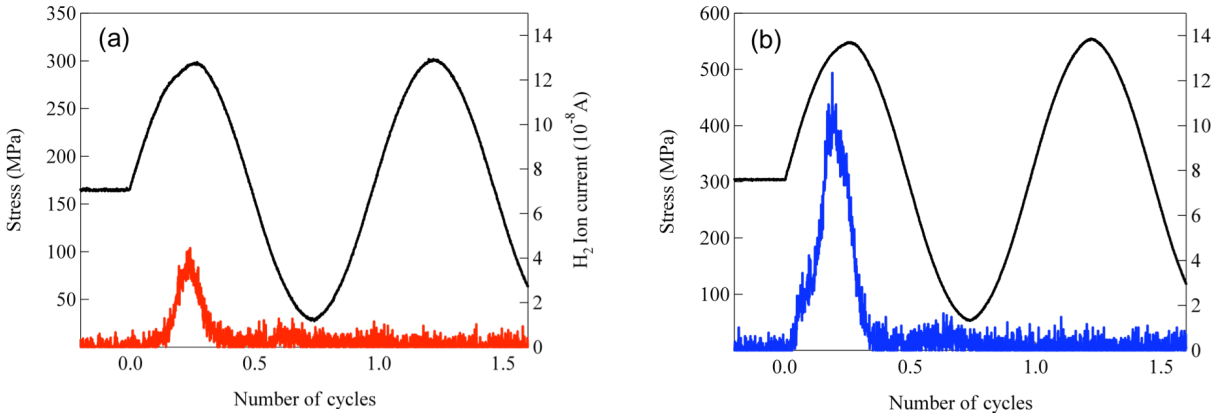

Fig.5 Hydrogen evolution behavior in the fatigue with a test frequency of 0.1 Hz, (a) 6061(Smooth), (b) 7075(Smooth).

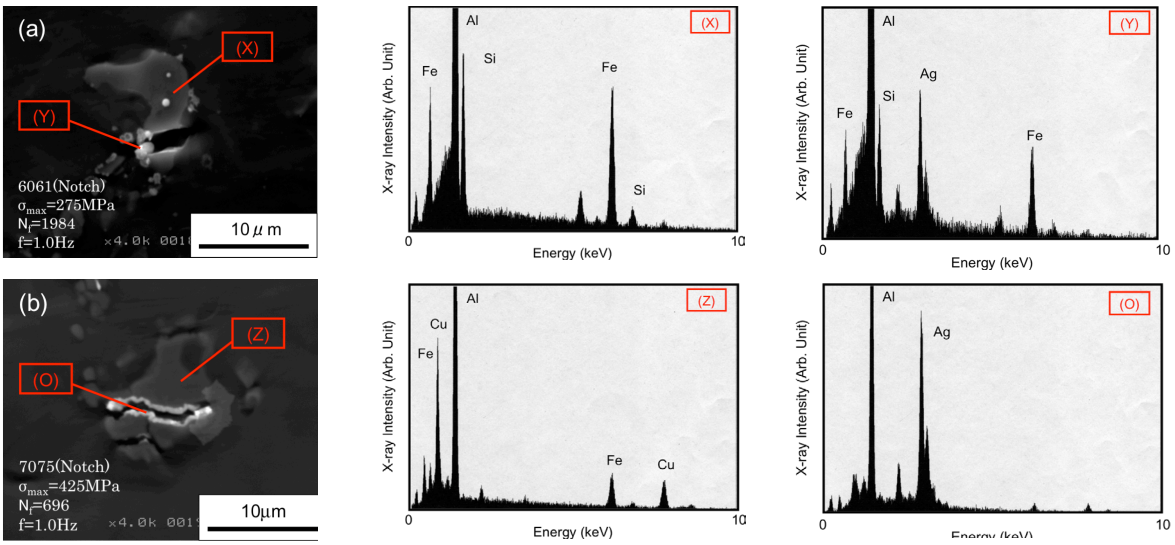

Fig.6 HMT/EDX images after the fatigue fracture in the specimens, (a) 6061(Notch), (b) 7075(Notch), in which the frequency was 1.0 Hz.

3.3 HMT

In order to identify the local hydrogen diffusion route during fatigue deformation, HMT was performed using the notched 6061 and 7075 alloys after the fatigue fracture as shown in Fig.6. The HMT showed that silver particles were accumulated around second phase inclusions such as AlFeSi phase in 6061 alloy and Al_7Cu_2Fe phase in 7075 alloy. The silver particles were preferentially observed at the inclusions with micro-cracks. Therefore, the hydrogen evolution during fatigue deformation should be partly related to the generation of the micro-cracks induced by the local fracture of the inclusions on the surface. This tendency is a similar manner as the case of the tensile test, as reported before [13].

Summary

Hydrogen evolution during the fatigue test in the 6061 and 7075 aluminum alloys was visualized by means of mass spectrometry in a UHV atmosphere and by HMT. The results obtained from this study are summarized as follows: (1) In the tensile test, hydrogen was highly evolved at the beginning of plastic deformation. (2) In the fatigue test, the peak of hydrogen evolution was observed in the early stage of the fatigue test. (3) The hydrogen evolution observed in the early stage of the fatigue test was connected with the variation of the stress amplitude. (4) The HMT revealed that hydrogen was locally evolved around second phase particles such as AlFeSi in the 6061 alloy and Al_7Cu_2Fe in 7075 alloy during the fatigue deformation.

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