Proceedings of the 12th International Conference on
Aluminium Alloys, September 5-9, 2010, Yokohama, Japan
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pp. 377-380

Behavior of Hydrogen invaded Aluminum Alloys from Environment

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In recent years, the fossil fuel exhaustion and global warming have become serious problems. As a way to solve these problems, the development of the fuel cell vehicles has been paid attention to. In the fuel cell vehicles, high-pressure hydrogen gas is stored in a container consisting of aluminum liner and surrounding fiber-reinforced plastic layer. To increase the mileage per filling, an aluminum alloy having higher strength than the currently used 6061 alloy is needed. It has been known that increase in the Si content in 6000 series aluminum alloy brings about increase in the strength. In this study, a 6061 aluminum alloy with Si content of highest level (6061HS) as well as a 6061 alloy with a typical composition has been subjected to slow strain rate technique (SSRT) tensile tests in a moist air to assess the resistance to hydrogen embrittlement, and also to thermal desorption spectroscopy (TDS) to investigate the hydrogen behavior. Moreover, to investigate the effect of grain size, 6061HS alloy specimen with coarse-grained microstructure has been also subjected to the SSRT tensile tests and TDS. In 6061HS-T6 even with coarse-grained microstructure, the resistance to hydrogen embrittlement is sufficiently high, although hydrogen is thought to invade to the specimen and to be trapped by dislocations when SSRT-deformed in the moist air.

Keywords: *6061 aluminum alloy, hydrogen embrittlement, hydrogen behavior, slow strain rate technique*

1. Introduction

In recent years, the fossil fuel exhaustion and global warming have become one of the most serious problems in the worldwide scale. There is a growing trend toward using hydrogen, which is the cleanest energy source, as one of the solutions. Especially, hydrogen fuel cell vehicles (FCVs) are being investigated and developed actively. To store hydrogen as the fuel, a high-pressure hydrogen container with an aluminum liner is installed in the FCVs. The only aluminum alloy approved as the liner in the Japanese standard is 6061 aluminum alloy for the maximum filling pressure of 35MPa [1]. Raising the maximum pressure to about 70MPa is scheduled to extend the mileage per filling, and an aluminum alloy with higher strength is demanded as the liner material for this purpose. Therefore, 6061 aluminum alloy that has been increased in the strength by raising the Si content up to the highest level within its composition range (6061HS) has been paid attention to.

Up to now there has been no report that mechanical properties of commercial aluminum alloys are deteriorated under the high-pressure hydrogen gas environment. In moist air environments, however, 7075-T6 alloy has been known to give rise to hydrogen embrittlement when subjected to the slow strain rate technique (SSRT) tensile tests [2]. Therefore, high strength aluminum alloy have a possibility of causing hydrogen embrittlement, and it is necessary to investigate the resistance to hydrogen embrittlement as well as the hydrogen behavior in the new candidate alloy to insure the safety. The SSRT tensile test in a moist air has been shown to be more severe than that in a hydrogen gas environment at 70MPa in terms of assessing hydrogen embrittlement susceptibility [3]. This is based on the extremely high hydrogen fugacity when metallic aluminum is exposed to water vapor and reacts as in Eq. 1.

$$2Al+3H_2O \rightarrow Al_2O_3+6H \,. \tag{1}$$

Thermodynamically, the fugacity of the hydrogen generated by this reaction is as high as about 6×10^{67}Pa [4], but surface oxide film is presumed to prevent continual reaction. In the SSRT tensile test the reaction of Eq. 1 takes place continually, allowing hydrogen to invade the material, so that the hydrogen embrittlement susceptibility can be assessed. On the other hand, thermal desorption spectroscopy (TDS) is an effective method to investigate the behavior of hydrogen in metallic materials. In this method, the amount of hydrogen and information on the trap site of hydrogen in a specimen can be obtained from the hydrogen desorption spectrum acquired by heating the specimen at a constant rate.

In this study, resistance to hydrogen embrittlement of a 6061HS will be evaluated by means of the SSRT tensile test in moist air, and the hydrogen behavior will be investigated by means of TDS, in comparison with those of a 6061 alloy with a typical composition. In addition, since grain coarsening frequently occurs in the neck portion of the actual liner, coarse-grained 6061HS has also been investigated.

2. Experimental Procedures

The specimens used in this study are a 6061 alloy with high Si content (6061HS), coarse-grained 6061HS (6061HS-CG) and a usual 6061 alloy (6061Ref) as a reference, in the form of 1mm thick sheets. The 6061Ref sheet was supplied from Furukawa-Sky Aluminum Corp. Their chemical compositions are shown in Table 1. All of them were T6-tempered : 6061HS solutioniged at 545°C, and then aged at 175°C for 8h; 6061Ref solutioniged at 460°C, and then aged at 120°C for 24h. Tensile test specimens with a gage portion of 12mm in length and 5mm in width were cut out from the sheets so that the tensile direction becomes vertical to the rolling direction. Both sides of the specimens were wet-ground up to #800, soaked in a 10%NaOH aqua solution, desmutted in a 10%HNO_3 aqua solution, rinsed with tap water and naturally dried. Preliminarily, the specimens were subjected to the tensile test at a usual strain rate of $1.39\times10^{-4}s^{-1}$ in dry nitrogen gas (DNG) atmosphere at ambient pressure with relative humidity (RH) of 5% or less, and the resultant tensile properties are shown in Table 2 with grain size, where the increase in strengths by raising Si content and the decrease in strength by coarsening grains are confirmed. The SSRT tensile test was conducted up to fracture at an initial strain rate of $6.94\times10^{-7}s^{-1}$ in two environments: moist air with RH of 90% (MA) and inert reference environment (DNG) at 30°C.

Some of the specimens were deformed by 3.5% at a slow strain rate of $1.39\times10^{-6}s^{-1}$ in the two environments, and samples of $25mm^2$ were cut from the gage portion. These samples as well as those cut out from the original sheets were subjected to TDS, which was carried out in the following way: (1) heating of the sample was started in an ultrahigh vacuum of 1.0×10^{-7}Pa or less; (2) the sample was maintained at 100°C for 30 min to remove adsorbed moisture; (3) the sample was heated up to about 570°C at a rate of 20°C /min, measuring the hydrogen desorption rate to obtain desorption spectrum.

Table 1 Chemical composition of specimens in mass%.

Specimen	Si	Fe	Cu	Mn	Mg	Cr	Ti	Al
6061HS 6061HS-CG	0.78	0.30	0.35	-	1.00	0.30	0.02	Bal.
6061Ref	0.63	0.29	0.30	0.05	1.00	0.20	0.02	Bal.

Table 2 Grain size and tensile properties of the specimens in DNG. Tensile direction, LT, and strain rate, $1.39\times10^{-4}s^{-1}$. Y.S.: 0.2% proof stress, U.T.S.: ultimate tensile strength, δ: elongation to failure.

Specimen	Grain size (μm)	Y.S. (MPa)	U.T.S. (MPa)	δ (%)
6061HS-T6	15	351	369	12.0
6061HS-T6-CG	171	343	362	11.9
6061Ref	-	303	331	14.3

3. Results and Discussion

Elongation to failure of the three specimens, tested at a strain rate of $6.94\times10^{-7}s^{-1}$ in each environment is shown in Fig. 1. The elongation decreases slightly by changing the atmosphere from DNG to MA in all the three specimens, and the extent of the decrease is largest in 6061HS-CG. In the 7075-T6 sheet, the elongation decreased by about half at a strain rate of $1.39\times10^{-6}s^{-1}$ by the same environment change [2] but no degradation in the elongation was detected in hydrogen gas atmosphere at 85MPa [5]. Thus the slight elongation decrease in the three specimens even in the 6061HS-CG is not regarded as any sign of hydrogen embrittlement.

The hydrogen desorption spectra of the deformed and undeformed specimens of 6061HS and 6061HS-CG are shown in Fig. 2. In all the six specimens, major peak is approximately in the temperature range from 470 to 570°C, which is thought to arise from the hydrogen trapped by second phase particles and microvoids. The onset of hydrogen desorption is at lowest temperature in the specimens deformed in MA for both alloys. This can be attributed to hydrogen trapping by dislocations introduced by the deformation since hydrogen trapped by dislocations is reported to be desorbed at about 400°C for a heating rate similar to that of the present experiment [4]. The desorption amount, the integral of the spectrum, is largest in the specimens deformed in MA for both alloys. Thus, hydrogen is deduced to invade the specimen from MA environment and to be trapped by dislocations. The effect of the deformation in DNG is different in the two alloys: the onset temperature of desorption and the desorption amount become lower and larger respectively by the deformation in DNG in 6061HS but opposite in 6061HS-CG. This might be due to the difference in the amount of impurity hydrogen that have been present before the deformation from specimen to specimen.

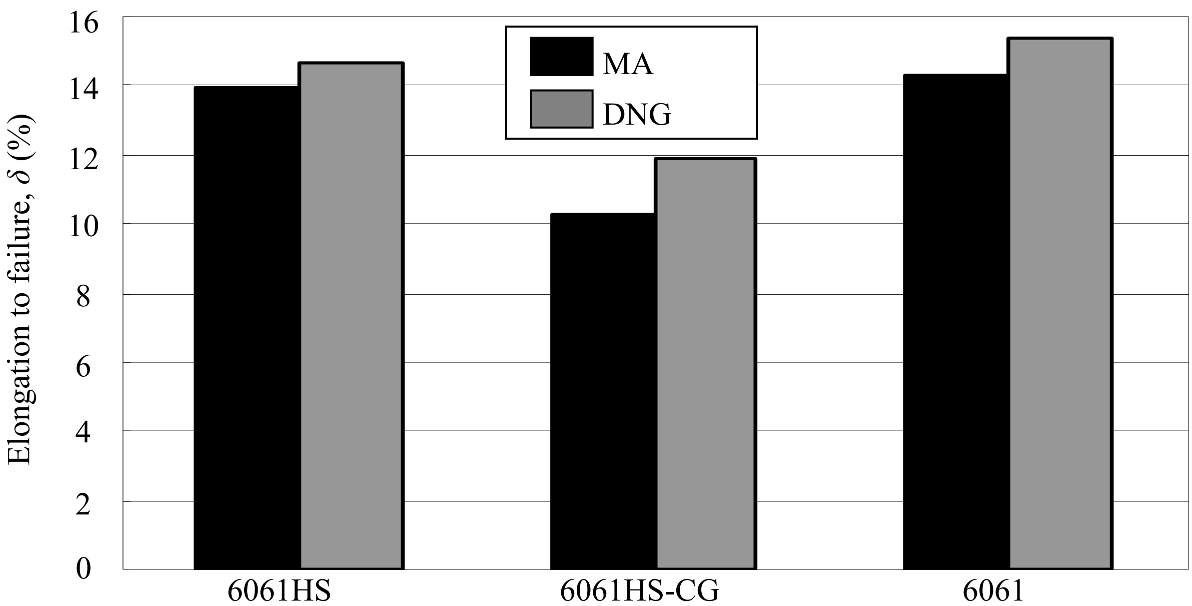

Fig. 1 Elongation to failure of the 6061HS, 6061HS-CG and 6061 specimens, tested at a strain rate of $6.94\times10^{-7}s^{-1}$ in the two environments. MA : moist air with RH of 90%, DNG: dry nitrogen gas with RH of 5% or less.

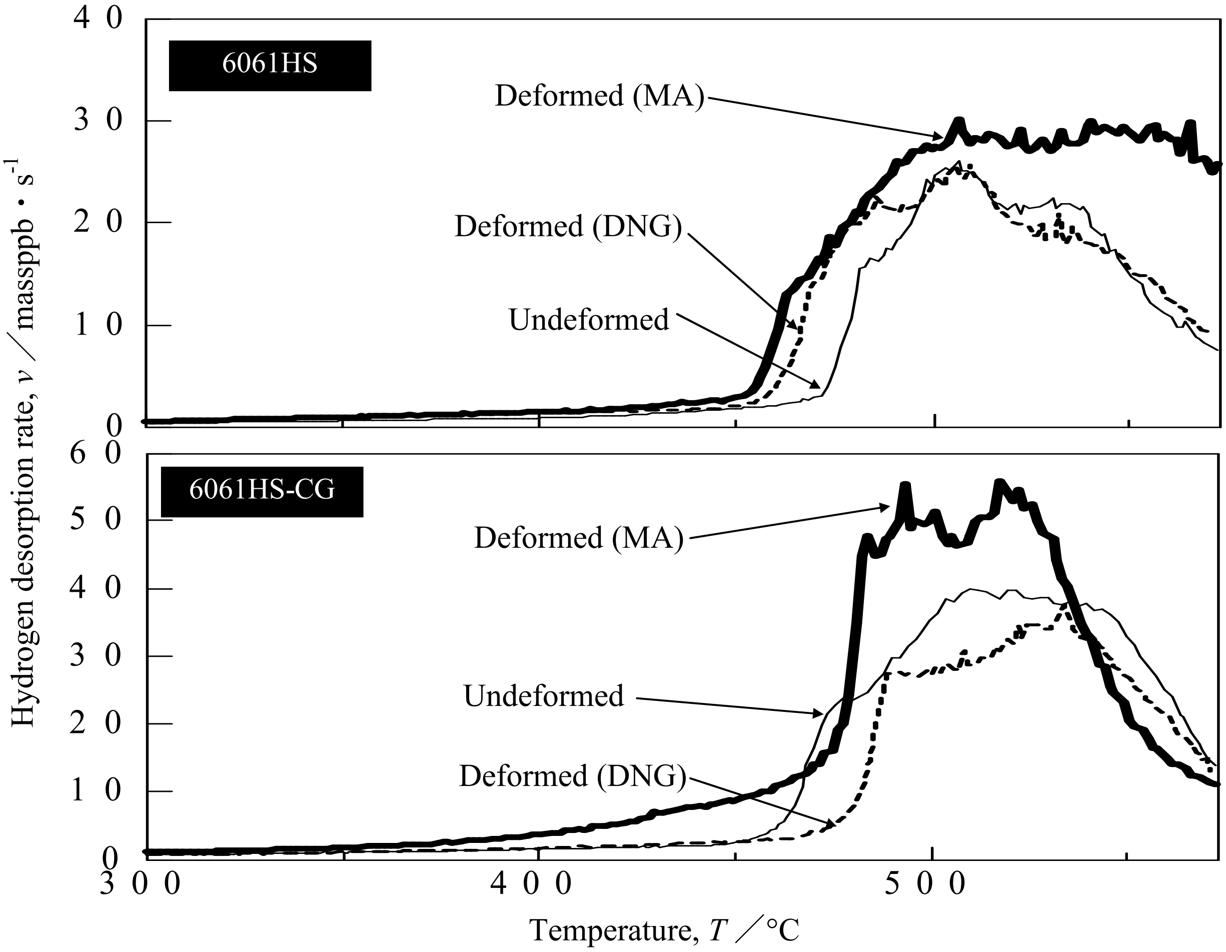

Fig. 2 Thermal desorption spectra (TDS) taken from 6061HS and 6061HS-CG specimens with and without tensile deformation by 3.5% at $1.39\times10^{-6}s^{-1}$ in the two environments (MA, DNG).

4. Summary

In 6061HS-T6, the resistance to hydrogen embrittlement is sufficiently high even with coarse-grained microstructure, although hydrogen is thought to invade to the specimen and to be trapped by dislocations when SSRT-deformed in MA.

Acknowledgment

The authors are grateful to Furukawa-Sky Aluminum Corp. that offered 6061-T6 sheets. This work has been made as a part of a NEDO Project, "Establishment of codes and standards for hydrogen economy society Fuel cell vehicles, distributed fuel cell system installed into houses, hydrogen infrastructures. Basic Research on Aluminum-Based Materials for Hydrogen"

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