Effects of Hydrogen on the Mechanical Properties of Pure Magnesium

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Tensile tests and Charpy impact tests have been performed on pure cast Mg with hydrogen concentrations of 16–35 mass ppm, where hydrogen was mainly segregated at triple junction of grain boundaries. Tensile properties were not affected by the hydrogen concentration, but crack formation at grain boundaries was enhanced by an increase in hydrogen concentration. The Charpy impact tests showed that the Mg with a higher hydrogen concentration exhibited a higher ductile-brittle transition temperature and that the temperature dependence of the Charpy impact energy was in good agreement with that of fractography. Thus, the segregation of hydrogen at grain boundaries likely induced the intergranular fracture of Mg. [doi:10.2320/matertrans.MC201009]

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1. Introduction

Magnesium alloys are promising light structural materials owing to their high specific strength and high specific stiffness. However, Mg alloys often exhibit low ductility and low fracture toughness at room temperature owing to few slip systems in the hexagonal close-packed structure.¹⁾ One of the effective ways for improving the ductility and fracture toughness of Mg alloys is grain refinement^{2,3)} because it promotes the prismatic $\langle a \rangle$ slips,⁴⁾ and it facilitates the creation of a large plastic zone ahead of the fracture precrack.^{5,6)} In addition, the control of texture⁷⁾ and the control of size and distribution of precipitates⁸⁾ are effective for the enhanced ductility and fracture toughness.

On the other hand, it is well known that the ductility and/or fracture toughness can be significantly reduced by the presence of a small amount of hydrogen in many metals.^{9–11)} For example, even a very low hydrogen concentration of less than 1 mass ppm has a harmful effect on the ductility of Fe.¹²⁾ Watanabe *et al.*¹³⁾ reported that the hydrogen concentration in a commercial pure Mg ingot is about 20 mass ppm at the atmospheric pressure and the room temperature. However, the solid solubility limit of hydrogen in Mg is only 0.08 mass ppm.¹⁴⁾ Thus, the commercial Mg ingots contain 250-fold excessive hydrogen, compared with the solid solubility limit.

Among the limited literatures, Chakrapani and Pugh¹⁵⁾ reported the relation between hydrogen concentration and mechanical properties of Mg-Al alloy, and revealed that hydrogen embrittlement is manifested by a deterioration of ductility in tensile tests, when the hydrogen concentration is set to be about 100 mass ppm. Noda *et al.*¹⁶⁾ investigated mechanical properties and microstructures of Mg-Al alloy subjected to hydrogenation disproportion desorption recombination (HDDR) phenomena, and suggested that the HDDR phenomena is effective for an increase in surface strength due to grain refinement. At least to our knowledge, there has been no studies on the effects of hydrogen on the mechanical properties of Mg, where hydrogen concentrations are the

same as those of the commercially available Mg ingots (several tens mass ppm). Mg is known to be a typical hydrogen storing metal, and it can absorb a large amount of hydrogen up to 7.6 mass% (66 at%), as MgH_2 .¹⁷⁾ On the other hand, hydrogenation/dehydrogenation phenomena of Mg is very slow and occurs only at very high temperature, indicating that small amount of residual hydrogen in Mg may affect mechanical properties and fracture mechanism due to its strong hydrogen bonding strength. Thus, in the present study, tensile tests and Charpy impact tests are performed on pure cast Mg with hydrogen concentrations from 16 to 35 mass ppm.

2. Experimental Procedure

Using an induction furnace, as-received pure Mg ingots of mass 150 g were melted at 1013 K in a graphite mold in Ar atmosphere. To control the hydrogen concentration, degassing of the Mg melts was carried out in Ar atmosphere at a pressure of 450 Pa for 5 and 10 min. Then, the melts were poured into rectangular steel molds with dimensions of $29 \times 49 \times 55 \text{ mm}^3$. For reference, a pure Mg without degassing was also prepared.

The chemical compositions of the Mg without degassing and after degassing for 5 min are summarized in Table 1, where carbon was detected by the combustion method (LECO CS444), hydrogen was detected by the inert gas fusion method using thermal conductivity detector (LECO RH402), oxygen was detected by the inert gas fusion method using non-dispersive infrared detector (LECO TC600), nitrogen was detected by the inert gas fusion method using thermal conductivity detector (LECO TC600), and the other elements were detected by the inductively coupled plasma-atomic emission spectroscopy (Shimadzu ICPS-8100). The hydrogen concentration was 35 mass ppm for the Mg without degassing and 23 mass ppm for the Mg after degassing for 5 min, respectively, and there was a large difference only in hydrogen concentration, as shown in Table 1. For the Mg degassed for 10 min, only the hydrogen concentration was measured, which was 16 mass ppm. Hereafter, the Mg specimens without degassing and those degassed for 5 and 10 min

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Table 1 Chemical compositions of the Mg without degassing and after degassing for 5 min.

	No degassing		degassing for 5 min	
	mass fraction	atomic fraction	mass fraction	atomic fraction
H	35 ppm	850 ppm	23 ppm	560 ppm
C	100 ppm	202 ppm	100 ppm	202 ppm
N	21 ppm	36 ppm	25 ppm	43 ppm
O	10 ppm	15 ppm	10 ppm	15 ppm
Al	180 ppm	160 ppm	190 ppm	170 ppm
Si	43 ppm	37 ppm	44 ppm	38 ppm
Ca	3 ppm	2 ppm	1 ppm	1 ppm
Mn	220 ppm	97 ppm	230 ppm	100 ppm
Fe	25 ppm	10 ppm	23 ppm	10 ppm
Ni	3 ppm	1 ppm	<1 ppm	<1 ppm
Cu	29 ppm	11 ppm	26 ppm	10 ppm
Zn	21 ppm	8 ppm	21 ppm	8 ppm
Mg	Bal. (99.931%)	Bal. (99.8571%)	Bal. (99.9307%)	Bal. (99.8843%)

Fig. 1 Microstructures of pure Mg ingot: (a) 35 ppm specimen, (b) 23 ppm specimen and (c) 16 ppm specimen, where the measured spot was indicated by broken line in Fig. 2.

are referred to as the 35 ppm specimen, the 23 ppm specimen and the 16 ppm specimen, respectively.

Figure 1 shows the optical micrographs of pure Mg ingots. The pure Mg ingots consisted of elongated grains, where the average grain size of short axis for the 16, 23 and 35 ppm specimens was 632, 503 and 674 μm , respectively; thus, there were minor differences in the grain size between the specimens. Hydrogen mapping in the 35 ppm specimen was performed using a secondary ion mass spectrometry (SIMS) to detect hydrogen segregation sites.

Round bar specimens with 2.5 mm gage diameter and 10 mm gage length were machined for tensile tests. Tensile tests were carried out at room temperature with an initial strain rate of $1.7 \times 10^{-3} \text{ s}^{-1}$. Also, the Charpy impact tests in the temperature range from 287 to 453 K were carried out with a Charpy impact machine (100J, Yonekura Seisakusho Co., Ltd.) using standard Charpy-V notch specimens ($10 \times 10 \times 55 \text{ mm}^3$). The ISO 148-1 recommendations¹⁸⁾ were followed during the testing. Fracture surfaces obtained by the tensile tests and the Charpy impact tests were observed using an optical microscope and a scanning electron microscope, respectively. Figure 2 shows the sampling sites for round bar specimen and Charpy-V notch specimen. In the tensile tests, the tensile direction was set to perpendicular to

Fig. 2 Macrostructure of pure Mg ingot (23 ppm specimen) and the sampling sites for round bar specimen and Charpy-V notch specimen.

Fig. 3 Hydrogen mapping using SIMS and related optical micrograph for the 35 ppm specimen: (a) hydrogen mapping and (b) optical micrograph.

the long axis of elongated grains. In the Charpy impact tests, the direction of crack propagation was set to perpendicular to the long axis of elongated grains.

3. Results and Discussion

The hydrogen mapping obtained using the SIMS for the 35 ppm specimen and the related optical micrograph are shown in Fig. 3, where the bright color means the higher intensity of hydrogen than the dark color, although the bright areas at the bottom left and at the top right are not the high intensity sites of hydrogen because of the pitted areas for pinpointing the location of observation. Hydrogen segregation was mainly observed at the triple junction of grain boundaries. Hydrogen segregation sites of the 35 ppm specimen was almost the same as that of the Mg-Al alloys with high hydrogen concentration,^{16,19)} where hydrogen segregation was observed at grain boundaries, in particular, at the triple junctions,¹⁹⁾ indicating that grain boundaries, in particular, triple junctions are the preferential segregation sites of hydrogen in pure Mg.

The nominal stress–nominal strain curves obtained from tensile tests at room temperature for the 16 and 35 ppm specimens are shown in Fig. 4. There were minor differences in the tensile properties of the specimens. Figure 5 exhibits the optical microstructures of the 16 and 35 ppm specimens

Fig. 4 Nominal stress–nominal strain curves obtained from tensile tests at room temperature for the 16 and 35 ppm specimens.

Fig. 6 The variation in Charpy impact energy as a function of temperature.

Fig. 5 Optical micrographs of the specimens deformed to failure in tensile tests: (a) 16 ppm specimen, (b) 35 ppm specimen, (c) 16 ppm specimen (contour of grain boundary is superimposed) and (d) 35 ppm specimen (contour of grain boundary is superimposed), where the white arrow in Fig. 5(a) indicates the fracture site in grain.

deformed to failure in the tensile tests. It is observed that more transgranular cracks (indicated by the white arrows) occurred in the 16 ppm specimen compared with the 35 ppm specimen regardless of the same tensile properties. It is suggested that more cracks occurred at the grain boundaries in the 35 ppm specimen compared with the 16 ppm specimen, and hydrogen segregation at grain boundaries observed in the 35 ppm specimen likely induced the intergranular cracking.

Figure 6 shows the temperature dependence of absorbed energy of pure Mg ingots by Charpy impact tests at various temperatures. As can be seen in Fig. 6, all the specimens exhibited a ductile-to-brittle transition. In the case of the 16 and 23 ppm specimens, those absorbed energy quickly decreased from 110 to 70 kJ/m² at 380 and 390 K, respectively. However, in the case of the 35 ppm specimen, the sharp transition was not observed, and its absorbed energy gradually decreased from 450 to 400 K. Obviously, the ductile-brittle transition temperature (DBTT) increased with increasing hydrogen concentrations, and the fracture mechanisms varied with hydrogen concentration. It is of interest to note that the DBTTs of Mg are higher than those for iron and steel, whose DBTTs are generally lower than 300 K.^{20–22)} The

high DBTT of Mg may be closely associated with an activity of non-basal slips, whose critical resolved shear stress (CRSS) significantly decreases with increasing temperature at around 423–523 K.¹⁾

Another interesting result is that both the 16 ppm and 35 ppm specimens exhibited a large elongation of about 10%, despite both the specimens had a much higher DBTTs compared with testing temperature of tensile tests. Ductility of Mg alloy at room temperature is known to be closely related to an activity of cross-slips,⁴⁾ which is thermally activated cross-slipping of screw dislocations from a basal plane to prismatic plane. Thus, it is suggested that the large strain rate dependence of cross-slip in Mg is probably ascribed to the differences in deformation characteristics between the tensile and impact tests.

The fracture surfaces of the 35 ppm specimens after Charpy impact tests at 287 and 453 K are shown in Fig. 7. The fracture surface tested at above DBTT was completely ductile, and the entire surface consisted of dimples. However, the cleavage surface, which consisted of flat facets, was observed at below DBTT. Figure 8 shows the ductility fracture ratio for the specimens as a function of test

Fig. 7 Fracture surfaces of the 35 ppm specimen after the Charpy impact tests: (a) 287 K and (b) 453 K.

Fig. 8 The variation in ductility fracture ratio as a function of temperature, where the ductility fracture ratio is the ratio of the ductile fracture area to the total area.

temperature, where the ductility fracture ratio is defined by the ratio of the ductile fracture area to the total area. The trend of ductile fracture ratio was in good agreement with that of the Charpy impact energy, suggesting that in the DBTT regime, the overall fracture process was governed by cleavage mode of failure.

The experimental results obtained in this study demonstrated that the segregation of hydrogen at grain boundaries induces the intergranular fracture of Mg, even when the hydrogen concentrations are several tens mass ppm. Kuramoto *et al.*¹⁹⁾ investigated hydrogen behavior during stress-corrosion cracking in an extruded AZ31 Mg alloy, whose grain size was several tens μm , and proposed that pipe diffusion caused by an accumulation of dislocations related to plastic deformation may promote an acceleration of hydrogen movement toward crack tip, resulting in brittle stress-corrosion cracking. Direct comparison between the results by Kuramoto *et al.*¹⁹⁾ and our results may be difficult because of the large differences in grain size and hydrogen concentration. However, it is suggested that the hydrogen embrittlement observed in our results is also likely attributed to segregation of hydrogen at grain boundaries due to stress concentration related to tensile and impact deformations, since there is no qualitative difference in the transition of fracture mode with variation in hydrogen concentration between them.

Nevertheless, there are still some unclear points in order to clarify the hydrogen embrittlement mechanism of Mg with several tens mass ppm. Direct observation of hydrogen segregation sites near fracture surface by using hydrogen microprint technique¹⁹⁾ and/or tritium autoradiography²³⁾ is still in progress. Further research is underway to understand the origin of hydrogen embrittlement in Mg.

4. Summary

The effects of hydrogen on the tensile and fracture properties of magnesium have been investigated by performing the tensile tests and the Charpy impact tests on pure cast Mg with hydrogen concentrations of 16–35 mass ppm. Hydrogen mapping by secondary ion mass spectrometry revealed that the hydrogen was mainly segregated at triple junctions of grain boundaries. As shown by tensile tests at room temperature, although the tensile properties were hardly affected by the hydrogen concentration, crack formation at grain boundaries was observed to be induced by an increase in hydrogen concentration. The Charpy impact tests in the temperature range from 287 to 463 K showed that the DBT temperature increased with increasing hydrogen concentration, and that the temperature dependence of the Charpy impact energy was in good agreement with that of fractography. Thus, it is suggested that the segregation of hydrogen at grain boundaries likely enhanced the intergranular fracture of Mg, even when the hydrogen concentration was several tens mass ppm.

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