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Su, Hang
Department of Mechanical Engineering, Kyushu University

Bhuiyan, Shahnewaz
Department of Mechanical Engineering, Kyushu University

Toda, Hiroyuki
Department of Mechanical Engineering, Kyushu University

Uesugi, Kentaro
Japan Synchrotron Radiation Institute (JASRI)

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Influence of intermetallic particles on the initiation and growth behavior of hydrogen micropores during high-temperature exposure in Al-Zn-Mg-Cu aluminum alloys

Hang Su\textsuperscript{a}, Md. Shahnewaz Bhuiyan\textsuperscript{a}, Hiroyuki Toda\textsuperscript{a}, Kentaro Uesugi\textsuperscript{b}, Akihisa Takeuchi\textsuperscript{b}, Yoshio Watanabe\textsuperscript{c}

\textsuperscript{a} Department of Mechanical Engineering, Kyushu University
\textsuperscript{b} Japan Synchrotron Radiation Institute (JASRI)
\textsuperscript{c} UACJ Corporation

Abstract

The X-ray tomography technique is employed to observe the effects of intermetallic compound particles on the nucleation and growth of hydrogen micropores at high temperatures in Al-Zn-Mg-Cu aluminum alloys. Hydrogen micropores are heterogeneously nucleated on particles during exposure at 748 K. Growth and coalescence of the hydrogen micropores are observed with increasing exposure time. Interactions between hydrogen micropores and particles have a significant influence on the growth and coalescence of hydrogen micro pores. The growth speed of hydrogen micropores, which are nucleated on spherical, small particles is faster than those on other nucleation sites.

Keywords X-ray microtomography, Synchrotron radiation, Hydrogen micropores, Al-Zn-Mg-Cu aluminum alloy
Recently, a series of research studies have been performed to improve the strength and fracture toughness of Al-Zn-Mg-Cu aluminum alloys [1-3]. However, increasing in strength leads to an increase in hydrogen embrittlement sensitivity of the precipitated strengthened aluminum alloys [4]. Young, et al. have revealed that the growth rate of hydrogen-induced cracks under the peak-aged condition is around twenty times higher than that of under-aged conditions in 7050 aluminum alloys [5]. Bhuiyan, et al. have compared the hydrogen-induced quasi-cleavage fracture behavior of Al-Zn-Mg-Cu aluminum alloys with different Zn contents, revealing that the hydrogen susceptibility is increased with the increase in Zn content [6].

A great number of hydrogen atoms are absorbed into aluminum alloys due to the destruction of the oxide film during high-temperature heat treatment, and the content of hydrogen is thereby much higher compared to the hydrogen solubility at room temperature [7,8]. With the help of thermal desorption spectroscopy, it has been clarified that supersaturated hydrogen atoms in aluminum alloys are partitioned to the trap sites such as interstitial lattices, vacancies, dislocations, solute atoms, precipitates, intermetallic particles and high-angle grain boundaries [9-12]. Hydrogen micropores are characterized as one of the hydrogen trap sites in aluminum alloys [9,13,14]. Toda, et al. have revealed that over 53 % of hydrogen atoms are sometimes trapped in micropores in Al-Mg aluminum alloys [13]. The initiation and growth of hydrogen micropores at high temperatures have been studied by several researchers in recent years. By applying the first-principles calculations, Liu, et al. have revealed that
hydrogen micropores are formed from hydrogen-vacancy clusters [15]. On the other hand, Toda, et al. have revealed with the help of the X-ray tomography technique that hydrogen micropores are heterogeneously initiated on the intermetallic particles in Al-Mg aluminum alloys. The growth of hydrogen micropores nucleated on particles is attributed to the high internal hydrogen pressure-induced creep deformation of the surrounding aluminum alloys [13]. In addition, hydrogen micropores nucleated on particles show premature growth under load and approximately 7-28 % of the dimples on the fracture surface are originate from hydrogen micropores [16].

Intermetallic compound particles, such as Al7Cu2Fe, Mg2Si and Al2CuMg, are observed in Al-Zn-Mg-Cu aluminum alloys [17-20]. According to the previous research, all of these particles can be characterized as the heterogeneous nucleation sites of hydrogen micro pores during high-temperature exposure [9,13,21]. Recently, Bhuiyan, et al. have revealed that approximately 51 % of hydrogen is trapped into hydrogen micro pores nucleated on particles in Al-Zn-Mg-Cu aluminum alloys, indicating their importance on hydrogen partitioning behavior [9]. On the other hand, hydrogen micro pores initiated on the particles might influence the damage evolution at the particles during loading. Su, et al. have revealed that hydrogen micro pores initiated on Al7Cu2Fe particles accelerate the formation of micro cracks under load through linkage with newly formed voids due to particle fracture [21]. In the present research, the aim is to reveal the formation behaviors of hydrogen micro pores in a practical Al-Zn-Mg-Cu aluminum alloy containing various intermetallic particles.
during high-temperature exposure. High-resolution X-ray tomography, technique which enables the visualization of the initiation, growth and annihilation of each micropore, is applied to clarify the above issue.

An as-cast Al-Zn-Mg-Cu aluminum alloy was used in the present research; its chemical composition was 10.00 Zn, 2.40 Mg, 1.50 Cu, 0.30 Fe, 0.30 Si, 0.15 Zr, 0.04 Ti and balance Al in mass %. To reveal the influence of intermetallic particles on the initiation and growth of hydrogen micropores during a homogenization treatment, ex-situ heating experiments were performed on the same specimen at 748 K for exposure times between 0 and 145.2 ks. A specimen 10 mm in length and 0.6 × 0.6 mm in cross-section was used for the X-ray tomography observation. A region 300 μm in height and 300 × 300 μm in cross section was extracted to investigate the nucleation sites of the hydrogen micropores.

The X-ray tomography experiment was performed at the BL20XU beamline in SPring-8. A monochromatic X-ray beam with a photon energy of 20 KeV, generated by a liquid nitrogen-cooled Si (1 1 1) double crystal monochromator, was applied for the 3D observations. An image detector was located 20 mm behind a specimen. The image detector was consisted of a 4000 (H) × 2624 (V) element CMOS camera, a single-crystal scintillator (Lu₂SiO₅: Ce) and a lens (20 ×). Eighteen hundred radiographs with scanning of 180°, were captured in 0.1 degree increments. The entire cross-section and an approximately 1024 μm region of the specimen were
captured on the CMOS camera. Image slices were reconstructed by the conventional filtered back-projection algorithm. The linear absorption coefficient (LAC) of 30-40 cm\(^{-1}\) fell within an 8-bit grayscale from 0-255 for a conversion process to 8-bit. The isotropic voxels in the reconstructed images were \((0.5 \, \mu m)^3\) in size.

Fig. 1 shows the 3D reconstructed images of the same specimen, including hydrogen micropores and intermetallic particles that are homogenized for different exposure times in Al-Zn-Mg-Cu aluminum alloys. The majority of the Al\(_2\)CuMg, Al\(_7\)Cu\(_2\)Fe and Mg\(_2\)Si particles are located along the grain boundaries in the as-cast Al-Zn-Mg-Cu aluminum alloys. The LAC values of the Mg\(_2\)Si, Al\(_2\)CuMg and Al\(_7\)Cu\(_2\)Fe particles range from -15 to 2, 30-40 and 27-35 cm\(^{-1}\), respectively. The Cu-bearing particles are hereinafter expressed as Al\(_2\)CuMg/Al\(_7\)Cu\(_2\)Fe due to the overlap of the LAC values. With increasing exposure time, Al\(_2\)CuMg/Al\(_7\)Cu\(_2\)Fe particles are gradually dissolved into the matrix while Mg\(_2\)Si particles remain in the materials. Deng, et al. have studied about the transformation of intermetallic particles during the homogenization process in Al-Zn-Mg-Cu aluminum alloys. After being homogenized at 743K for more than 24 h, Al\(_2\)CuMg particles dissolve into the matrix, and only irregular Al\(_7\)Cu\(_2\)Fe particles remain along the grain boundaries [18]. Although it was impossible to separate Al\(_2\)CuMg and Al\(_7\)Cu\(_2\)Fe particles in the present work, it can still be inferred that only Al\(_7\)Cu\(_2\)Fe particles remain in the matrix after long time exposure.
The initiation, growth and annihilation of hydrogen micropores during high-temperature exposure can also be seen in Fig. 1. In the as-cast condition, the shrinkage cavities with complex shapes are seen to be located at the interface between the intermetallic particles and the matrix. During the homogenization treatment at 748 K for 0.8 ks and 1.9 ks, the shrinkage cavities gradually become spherical, as shown in pore A in Fig. 1a-c). Instead, small hydrogen micropores are heterogeneously nucleated at high number density on the intermetallic particles, as shown in Fig 1. b-c), making the spatial distribution of hydrogen micropores relatively homogeneous. With the increase in exposure time, the hydrogen micropores continue to grow, as shown in Fig 1. d-f). During the homogenization treatment at 748 K, pore A gradually grows up and then coalesces with neighboring hydrogen micropores after being exposed for 4.5 ks. Pore B shows an independent growth without coalescence up to 145.2 ks. Pore C is initiated on Al$_2$CuMg/Al$_7$Cu$_2$Fe particles at 4.5 ks and annihilates after being exposed for 145.2 ks. According to Toda, et al., Ostwald ripening is the growth mechanism of hydrogen micropores, and small hydrogen micropores gradually annihilate with the increase in exposure time [13]. It is worth noting that hydrogen micropores exhibit octahedral shapes consisting of eight {111} planes that are energetically stable in aluminum alloys [13] after being exposed to 748 K for 145.2 ks, as shown in Fig 1. f).

Fig. 2 shows cross-sectional images, showing intermetallic particles and hydrogen micropores that are observed after being exposed at 748 K for 10.8 ks, 25.8 ks, 61.2
For the irregular, large $\text{Al}_2\text{CuMg}/\text{Al}_7\text{Cu}_2\text{Fe}$ particles, hydrogen microholes tend to be initiated on the tips of these particles, as shown as particle A in Fig. 2d). With the increase in exposure time, particles gradually dissolve into the matrix, and hydrogen microholes continue to grow. The coalescence of hydrogen microholes is observed after being exposed at 748 K from 25.8 ks to 145.2 ks, as shown as pores A, B and C in Fig. 2a). Closely spaced hydrogen microholes are prone to form larger pores through coalescence partly due to the superposition of hydrostatic strain fields among neighboring pores [22]. In contrast, almost no coalescence of neighboring hydrogen microholes is observed for those nucleated on the tips of $\text{Al}_2\text{CuMg}/\text{Al}_7\text{Cu}_2\text{Fe}$ particles, as shown on particle A in Fig. 2d). It can be inferred that the remaining particles restrain creep deformation [23], thus impeding the coalescence of neighboring hydrogen microholes.

Fig. 3 shows the results of a 3D quantitative analysis. The number density of hydrogen microholes shows a rapid increase up to 4.5 ks, remains unchanged from 4.5 ks to 10.2 ks, and then begins to decrease during exposure from 10.8 ks to 145.2 ks, as shown in Fig. 3a). The average diameter of the hydrogen microholes increases with the increase in exposure time, as shown in Fig. 3a). The size distribution of the hydrogen microholes is narrow, with a mean diameter of approximately 2 $\mu$m between the as-cast state and 0.2 ks exposure time, as shown in Fig. 3b). Although the most frequently observed size range is not so remarkably different (e.g., 4-6 $\mu$m for 145.2 ks), very coarse microholes of approximately 10 $\mu$m or even larger are observed due
mainly to the coalescence after 25.8 ks.

The nucleation sites of hydrogen micro pores are summarized in Table 1, with respect to the species of the particles. The ratio of hydrogen micro pores initiated on Al$_2$CuMg/Al$_7$Cu$_2$Fe particles is 36.5 %, which is almost 3.5 times higher than that of Mg$_2$Si particles. It can be seen that the heterogeneous nucleation of hydrogen micro pores on particles might be influenced by the chemical composition of the intermetallic particles, as well as their size and morphology. A thermal expansion mismatch between the intermetallic particles and the matrix leads to the generation of hydrostatic stress during the cooling process of casting. Using a finite element method simulation, Christman, et al. have revealed that compressive hydrostatic stress is uniformly distributed around spherical particles while hydrostatic tension is generated around corners and sharp edges in the case of angular whiskers [24]. Although the thermal expansion coefficients of such complex intermetallics are not known, the difference in the nucleation behavior in Table 1 is at least attributable to the more complex and irregular shape of the Al$_2$CuMg/Al$_7$Cu$_2$Fe particles compared to the Mg$_2$Si particles.

Several papers have also reported similar heterogeneous nucleation of hydrogen micro pores on particles. For example, Shewmon has observed that hydrogen micro pores are heterogeneously nucleated on the oxide inclusions that are located along grain boundaries in a carbon steel [25]. Lee, et al have clarified that hydrogen
Micropores tend to be initiated between columnar dendrites during solidification in Al-Cu aluminum alloys [26]. On the other hand, several studies have reported that the formation of molecular hydrogen occurs in vacancies, hydrogen-vacancy clusters can be considered as the preliminary stage of hydrogen micro pore nucleation [15,27]. Laureys, et al. have revealed that the formation of hydrogen blisters is promoted by deformation-induced defects such as dislocations and nano voids [28]. Matsumoto, et al. have concluded using the first principle simulations that the separation of hydrogen atoms from aluminum as molecular hydrogen is the most stable state, whereas the absorption of atomic hydrogen on the surface is slightly less stable [29]. Since even a mono vacancy can trap several hydrogen atoms in it [29], hydrogen micropores can be formed without particles as nucleation sites, originating from hydrogen trapping at vacancies [27]. In such cases, the formation mechanism of the hydrogen micropores is homogeneous nucleation. According to the hydrogen-enhanced stabilization of vacancy mechanism, hydrogen atoms trapped at vacancies drastically decrease the diffusivity of vacancies [30]. This implies that the migration of vacancies with hydrogen and the resulting coalescence to form hydrogen micropores is less apt to occur. In the present research, it has been confirmed that over 60 % of the hydrogen micropores nucleate heterogeneously on the intermetallic particles. There is also no evidence within the present research that vacancies are involved in the formation of hydrogen micropores.

Fig. 4 shows the influence of diameter and sphericity on the growth of the hydrogen
micro pores for each intermetallic particle. The diameters of Al$_2$CuMg/Al$_7$Cu$_2$Fe particles with hydrogen micro pores range from 2 to 12 μm, as shown in Fig. 4a). In contrast, the size of Mg$_2$Si particles with hydrogen micro pores is smaller (2-6 μm) than that of Al$_2$CuMg/Al$_7$Cu$_2$Fe particles, as shown in Fig. 4b). For the hydrogen micro pores that are nucleated on Al$_2$CuMg/Al$_7$Cu$_2$Fe particles, although the diameters of the nucleation sites for both pore A and pore B are approximately 4 μm, the growth speed of pore A, which was nucleated on a spherical particle, is four times higher than pore B, which was nucleated on an angular particle, as shown in Fig. 4a). The growth velocities of pores C, D and E, which initiated on the angular particles with similar sphericities (approximately 0.3), are approximately 0.05 μm/s regardless of the increase in diameter. For the hydrogen micro pores initiated on the Mg$_2$Si particles, the growth speed of the pores nucleated on spherical particles is higher than that of those on angular particles, as shown in Fig. 4b).

The gas pressure of a hydrogen micro pore is in thermal equilibrium with the surface tension of the aluminum matrix, based on equation 1 [31]:

\[ P = \frac{4\gamma}{d} \]  

(1)

where \( P \) is the internal gas pressure, \( \gamma \) is the surface tension of aluminum and \( d \) is the diameter of a pore. The internal gas pressure of a typical hydrogen micro pore (1 μm) is approximately 4 MPa under the assumption of \( \gamma = 1.16 \text{ N m}^{-1} \) [22]. Therefore, it can be inferred that the growth of hydrogen micro pores under high temperatures is induced by the creep deformation of the surrounding aluminum matrix caused by the
high internal gas pressure [13,22]. Kawabata, et al. have performed a creep test at 673 K for both angular SiC particle-reinforced and spherical Al$_2$O$_3$ particle-reinforced aluminum alloys, revealing that the creep rate of the Al$_2$O$_3$/Al composite is around two orders of magnitude higher than that of the SiC/Al composite [32,33]. Rösler, et al. have proposed that angular Al$_4$C$_3$ particles suppress the detachment of dislocations more efficiently than spherical Al$_2$O$_3$ particles do, thus impeding the dislocation detachment-induced creep at high temperatures [34]. In addition, for the localized creep deformation in the present material, it is worth noting that the hydrostatic stress concentration generated on angular particles, especially on corners and sharp edges, might induce high constraint on the matrix, making creep flow more difficult. It seems most likely that a similar constraint of creep deformation occurs around the angular intermetallic particles during high-temperature exposure in the aluminum alloy is investigated.

In conclusion, our investigations using high-resolution X-ray tomography have revealed the influence of intermetallic particles on the initiation and growth of hydrogen micropores at high temperatures in the Al-Zn-Mg-Cu aluminum alloys. Hydrogen micropores are heterogeneously nucleated on intermetallic particles, indicating that hydrogen micropores need particles as their nucleation sites. It seems that the initiation of micropores on particles is influenced by the size and morphology of the particles. The growth of hydrogen micropores is dominated by the creep deformation of the matrix around the micropores due to their high internal gas
pressure. The growth speed of hydrogen nucleated on angular particles is slower than that of those initiated on spherical particles.

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References

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Table captions

Table 1 Nucleation behavior of hydrogen micropores on different intermetallic particles
Figure captions

Fig. 1 3D rendered images of an identical region in the material exposed at 748 K for:
- a) 0 ks, b) 0.8 ks, c) 1.9 ks, d) 4.5 ks, e) 25.8 ks f) 145.2 ks. Hydrogen micropores are shown in red, Al2CuMg/Al7Cu2Fe particles are shown in blue and Mg2Si particles are shown in green.

Fig. 2 Cross-sectional images of an identical region in the material exposed at 748 K for: a) 10.8 ks, b) 25.8 ks, c) 61.2 ks, d) 145.2 ks.

Fig. 3 3D quantitative analysis of hydrogen micropores during exposure at 748 K; a) Variations in average diameter and number density, b) Size distributions of hydrogen micropores.

Fig. 4 Growth speed of hydrogen micropores nucleated on the intermetallic particles; a) Al2CuMg/Al7Cu2Fe particles, b) Mg2Si particles.
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