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Hydrogen trapping in an Al–2.1 wt % Li alloy

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Hydrogen trapping in an Al–2.1 wt % Li alloy aged up to typical stages in the age-hardening curve, has been studied by measuring the tritium release rate after charging. The distribution of hydrogen in the aged alloy has been studied by tritium electron microautoradiography. It has been found that the coherent δ′ precipitate and the incoherent δ precipitate act as a trapping site for hydrogen, while the semi-coherent δ′ precipitate does not trap hydrogen. A dislocation has been found to be capable of trapping hydrogen, while hydrogen trapping by the grain boundary has not been observed.

1. Introduction

Aluminium–lithium alloys have recently attracted much attention for applications as aerospace materials, because these alloys exhibit classical age-hardening behaviour with lightweight and high elastic modulus as well as superior mechanical properties [1–3]. However, low ductility and stress-corrosion cracking of the alloys have been observed [4]. To overcome these problems, many attempts have been made to survey chemical compositions and heat treatments of the alloys [1–3]. Study of hydrogen behaviour in the alloys is indispensable, because hydrogen plays an important role in the ductility of the alloys, and because the hydrogen content in the alloys is more than ten times of that in other aluminium alloys [5].

The precipitation process of a supersaturated Al–Li alloy is known from earlier conventional electron microscopic works [6–8] to be: supersaturated solid solution → sphere-like metastable precipitate (δ′ phase, Al_3Li) → granular equilibrium precipitate (δ phase, Al_3Li). On the other hand, based on differential scanning calorimetry and resistivity measurements of the alloys, Nozato and Nakai [9] and Ceresara *et al.* [10] have proposed early stages of disordered Guinier–Preston (GP) zone → ordered GP zone → short-range-ordered metastable precipitate (δ″ phase, Al_3Li) before the precipitation of δ′ phase. Using thermal analysis and transmission electron microscopy for the study of precipitation phenomena and structural changes in Al–Li alloys, Takahashi and Sato [11] have found the precipitation process to be: supersaturated solid solution → lithium cluster (GP (1)) → short-range order (GP (2)) → coherent metastable δ′ phase → semi-coherent metastable δ′ phase → equilibrium δ phase. A recent study on the early stage of phase decomposition of the alloy by atom-probe field-ion microscopy and transmission electron microscopy [12] has shown that the δ′ phase with the stoichiometric lithium concentration is already precipitated in the as-quenched stage. Therefore, wide variations of metallographic microstructure, as well as lattice defects such as dislocations and grain boundaries, can be formed by ageing a supersaturated alloy. Thus, it is very interesting to examine the interactions between hydrogen and each of the microstructures.

Tritium electron microautoradiography is a unique and useful technique which can provide visual information on the interrelationship between hydrogen distribution and microstructure [13]. Tritium emits only low-energy β-rays with a continuous energy spectrum (maximum energy 18.6 keV) with a half-life of 12.3 year. The maximum range of the β-rays of tritium through photographic emulsion (silver bromide) and aluminium is 2.5 and 2.7 μm, respectively, and 99% of the energy is absorbed on passing through these materials by about 0.4 μm [14]. Thus, the spatial resolution for the tritium distribution in the specimen of the autoradiograph is very high. A sensitive film is adhered to the specimen and exposed to the β-rays from tritium charged in the specimen. The film is then developed, and the distribution of silver grains in the film is examined by electron microscopy. So far, this technique has been applied by us to pure aluminium [15] and aluminium alloys such as Al–Mg–Si[15–17], Al–Zn–Mg[18] and Al–Cu[15,17] to identify the trapping and repelling sites of hydrogen in them. Recently, Okada *et al.* [19] have used this technique to study the hydrogen segregation in Al–3 wt % Li alloy and showed that hydrogen exists at the interfaces between the matrix and the δ phase precipitated at grain boundaries in the alloy aged at 190 °C for 173 ks. However, the interaction between hydrogen and δ′ precipitate is not known.

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In the present work, first the age-hardening curve of the alloy at 200 °C has been determined. Secondly, the intensity of trapping hydrogen in the specimens aged up to typical stages in the age-hardening curve has been studied by measuring the tritium release rate after charging. Finally, the interrelationship between hydrogen distribution and microstructures with lattice defects and precipitates has been investigated by tritium electron microautoradiography.

2. Experimental procedure

An ingot of Al–2.1 wt % Li alloy was prepared by melting an Al–Li master alloy containing 18.5 wt % Li together with aluminium blocks (99.999% purity) in an argon atmosphere using a steel mould, 14 mm diameter, for the cast. The Al–Li master alloy was supplied by Sumitomo Light Metal Industries Ltd. The main impurities in the ingot were Fe 0.02 wt % and Si 0.02 wt %. The ingot was machined to a rod 11 mm diameter and then homogenized at 500 °C for 150 h. The rod was hot-forged at 500 °C to a sheet 3 mm thick and again annealed at 500 °C for 1 h and finally cold-rolled to a foil 0.2 mm thick. Foil specimens 5 mm × 5 mm × 0.2 mm in size were sealed in a glass tube with argon gas and were solution heat-treated at 500 °C for 2 h and then quenched into ice–water. Subsequently, the specimens were aged at 200 °C in an oil bath. After ageing, the specimens were kept in a refrigerator at – 10 °C. The hardness of the specimens was measured by a Vickers micro-hardness tester at room temperature with 200–1000 g loading. All the readings were averaged on eight impressions.

Tritium and hydrogen were charged into the specimens at room temperature by the cathodic charging method. The electrolyte was 0.5 N H_2SO_4 aqueous solution containing tritium of 3.7×10^{13} Bq m^{-3}, the current density and charging time being 100 A m^{-2} and 1 h, respectively. After charging, each specimen was rinsed with water and with ethyl alcohol and put into a scintillator solution (Scintisol 500) within 5 min after the charging and held in it for 24 h. The radioactivity of tritium released from the specimen into the scintillator solution was measured for 2 h by a liquid scintillation counter.

For the tritium electron microautoradiography, tritium and hydrogen were charged into the specimens by the same method as above. After charging, each specimen was kept at – 10 °C for 3 days to release excess hydrogen and to attain an equilibrium distribution of hydrogen. Discs, 3 mm diameter, were cut from the specimen and polished into thin foils by the twin-jet method using a solution of 7 parts C_2H_5OH and 1 part $HClO_4$ as an electrolyte at 0 °C. The electrolytic voltage was 30 V. A sensitive film made of a mono-layer of fine silver bromide grains, 0.06 μm diameter, was prepared on collodion thin films by the wire-loop method from a nuclear photographic emulsion (Konica NR-H2). One or two drops of isoamyl acetate were put on the specimen to adhere the sensitive film to the specimen. The set of the sensitive film and the specimen was kept in a dark box maintained at – 10 °C for 6 days to expose the sensitive film to the β-rays emitted from tritium in the specimen.

After exposure, the sensitive film on the specimen was developed to turn the silver bromide grains exposed by the β-rays into metallic silver grains. Thus, information on the distribution of hydrogen in the specimen was obtained by observing the distribution of silver grains in the autoradiograph. To make simultaneous observation of both the hydrogen distribution and the microstructure of the specimen, the specimen and the autoradiograph adhered to it were observed at the same time by transmission electron microscopy (TEM, Jeol-200B) at an accelerating voltage of 200 kV.

3. Results and discussion

The age-hardening curve of the Al–2.1 wt % Li alloy aged at 200 °C is shown in Fig. 1. The hardness value of the as-quenched specimen was 45. After an incubation time of about 20 s, the hardness begins to increase gradually and has a plateau of about 85 during ageing for 200–5000 s. Beyond the plateau region, the hardness increases again to a value of about 110, which forms a second plateau including a maximum at the ageing time of 100 ks, and finally decreases gradually with ageing time to an over-ageing region. According to studies on the precipitation process of the alloys [6–12], the first hardness plateau is due to the formation of coherent δ′ precipitates, and the second plateau, including the maximum of hardness, is due to the formation of semi-coherent δ′ precipitates. The over-ageing after the maximum is due to the formation of δ precipitates.

Radioactivity of released tritium from the as-quenched specimen and also from the aged specimens at typical stages is shown in Fig. 2. Tritium charging for all the specimens was carried out under the same conditions. As shown in Fig. 2, the radioactivities of tritium released from the as-quenched specimen and from the specimen aged for 100 ks are much higher than those from specimens aged for 1 and 500 ks. High radioactivity of released tritium from a specimen means that most of the previously charged tritium is released and only a part of the tritium remains in the specimen, and vice versa. Fig. 2 shows that the intensities of trapping hydrogen in both the specimens aged

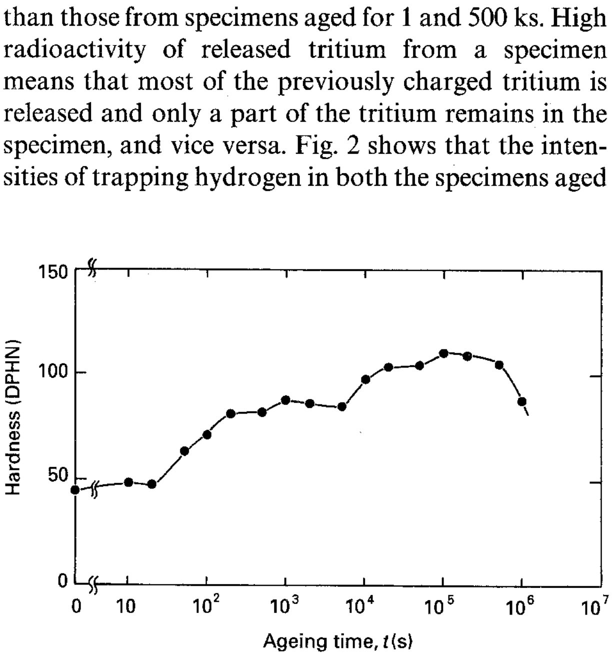

Figure 1 Age-hardening curve of Al–2.1 wt % Li alloy aged at 200 °C after quenching from 500 °C.

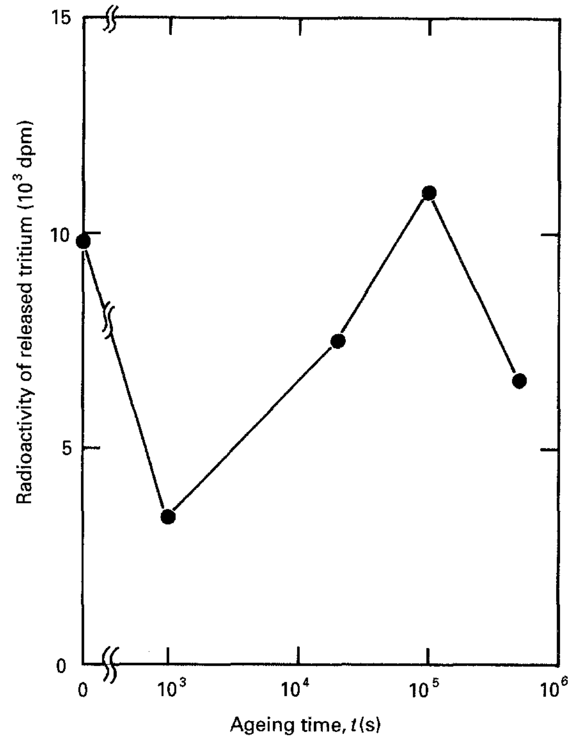

Figure 2 Radioactivity of tritium released from Al–2.1 wt % Li alloy measured by a liquid scintillation counter.

for 1 and 500 ks are strong, while on the other hand, those in the as-quenched specimen and in the specimen aged for 100 ks are weak. Thus, in the as-quenched specimen, it appears that vacancy-rich lithium clusters [9–11] do not trap hydrogen. The trapping power in the aged specimens increases with the formation of coherent δ′ precipitates. According to Tamura *et al.* [20], the misfit parameter of the coherent δ′ phase is −0.3%. Therefore, the coherent δ′ precipitates cause a tensile elastic stress field in the matrix around them. This tensile stress field acts as a trapping site for hydrogen, as in the case of the GP zones in Al–Cu alloys [15, 17]. However, as shown in Fig. 2, with the transition from the coherent δ′ precipitate to the semi-coherent δ′ precipitate, the trapping power decreases. During the transition of the coherency of δ′ precipitate with the matrix, the coherent tensile strain around the precipitate is released owing to the formation of interfacial dislocations [11], and the trapping power decreases. Finally, the trapping power increases again with the formation of δ precipitates in the overaged state. Because the equibrium δ precipitate is incoherent with the matrix lattice, many interfacial dislocations exist around it. The interfacial dislocations may trap hydrogen and accumulate it on the interfaces between the δ precipitates and the matrix lattice, as in the cases of β precipitate in Al–Mg–Si alloys [15–17] and η precipitate in Al–Zn–Mg alloys [18].

Fig. 3 shows a tritium electron microautoradiograph of Al–2.1 wt % Li alloy aged at 200 °C for 20 ks after quenching. Sphere-like δ′ precipitates with a high density are observed. However, silver grains are only rarely seen. This suggests that the δ′ precipitates have zero or very weak trapping power for hydrogen.

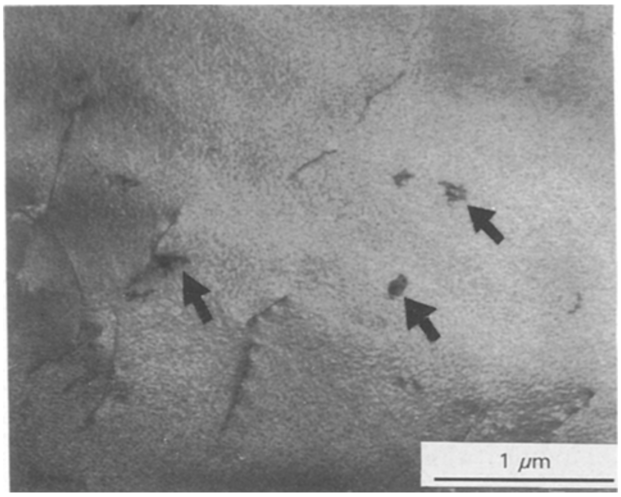

Figure 3 Tritium electron microautoradiograph of Al–2.1 wt % Li alloy aged at 200 °C for 20 ks after quenching. A few silver grains are observed at the end of dislocation, as shown by the arrows.

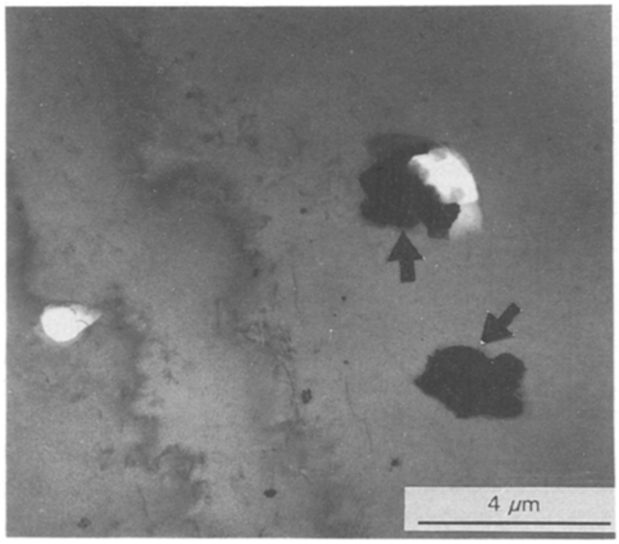

Figure 4 Tritium electron microautoradiograph of Al–2.1 wt % Li alloy aged at 200 °C for 20 ks after quenching. Silver grains are observed at the interface between the matrix and the unresolved δ precipitates, as shown by arrows. White parts are holes from which δ precipitates have fallen off by mishandling of the specimen.

This is consistent with the high intensity of released tritium from the specimen, as shown in Fig. 2, and at this stage the coherent strain between the δ′ precipitate and the matrix has been fairly released [11]. A few silver grains in Fig. 3 are located at the terminals of the dislocation lines which act as a trapping site for hydrogen and also acts as a short-circuiting diffusion path for hydrogen [15, 17].

Fig. 4 shows another microautoradiograph of the same heat-treated specimen as that shown in Fig. 3. Silver grains are observed at the interface between the matrix and the large δ precipitate which was unresolved by the solution heat treatment of the present experiment. The equilibrium δ precipitate is incoherent with the matrix lattice. Hydrogen must be trapped by the misfit dislocations around δ precipitates and is accumulated on the interfaces between the precipitates

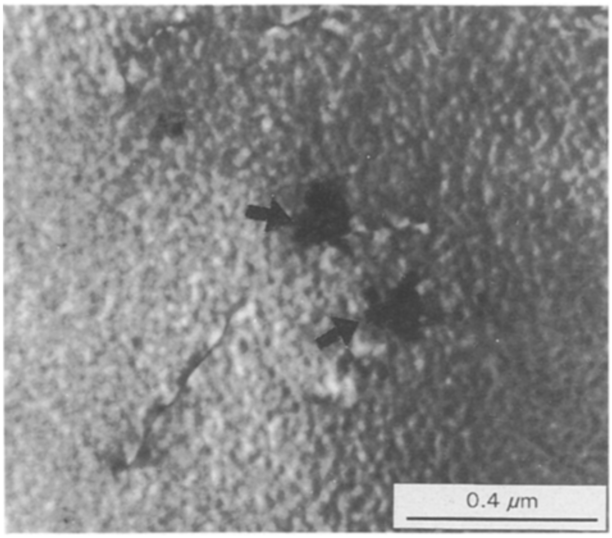

Figure 5 Tritium electron microautoradiograph of Al–2.1 wt % Li alloy aged at 200 °C for 100 ks after quenching. Silver grains are observed at the end of dislocation, as shown by arrows.

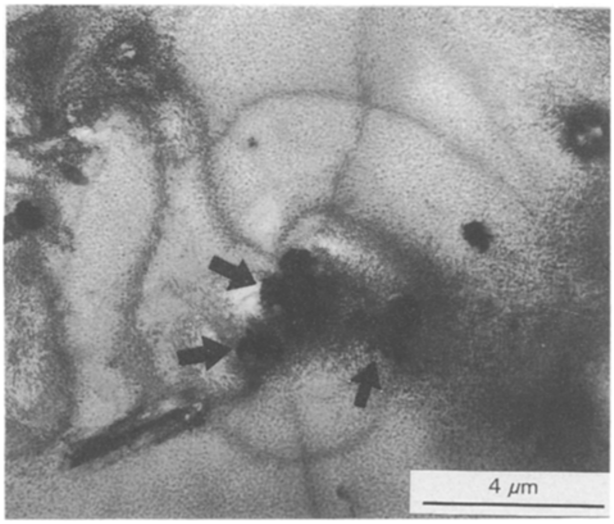

Figure 6 Tritium electron microautoradiograph of Al–2.1 wt % Li alloy aged at 200 °C for 500 ks after quenching. Silver grains are observed at the interface between the matrix and δ precipitates, as shown by arrows.

and the matrix. Furthermore, Okada *et al.* [19] have suggested the hydride formation of δ precipitate; however, in the present experiments the hydride formation cannot be confirmed.

Fig. 5 shows a tritium electron microautoradiograph of Al–2.1 wt % Li alloy aged at 200 °C for 100 ks after quenching to attain the state of maximum hardness (Fig. 1) by the precipitation of semi-coherent δ' phase. The δ' precipitates are observed with very high density, while only a few silver grains are observed at the end of the dislocation lines. In this stage the coherent strain around the semi-coherent δ' has been released [11], and then the trapping power is very weak or negligible (Fig. 2).

Fig. 6 shows a tritium electron microautoradiograph of Al–2.1 wt % Li alloy aged at 200 °C for 500 ks after quenching to obtain the over-aged state (Fig. 1). Silver grains are observed at the interface between the matrix and δ precipitate, as shown by arrows. The interface acts as a trapping site for hydrogen in accordance with the decrease in the released tritium at the over-aged stage (Fig. 2). Furthermore, no silver grain at the grain boundary without precipitates is observed in the present experiments. This means that the high-angle grain boundary in the matrix has zero or very weak trapping power for hydrogen.

4. Conclusions

1. Dislocations in aluminium alloys act as trapping sites for hydrogen and also act as short-circuiting diffusion paths for hydrogen.
2. The coherent metastable δ' precipitate traps hydrogen but the semi-coherent metastable δ' precipitate does not.
3. The interface between the matrix and δ precipitate acts as a trapping site for hydrogen.
4. The high-angle grain boundary in the matrix itself has zero or very weak trapping power for hydrogen.

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