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ANALYSIS OF HYDROGEN BEHAVIOR IN AN Al-Li ALLOY BY TRITIUM ANALYSIS AND TRANSMISSION ELECTRON MICROSCOPIC AUTORADIOGRAPHY

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Abstract

The effect of hydrogen on the properties Al-Li alloys were investigated by using three tritium tracer techniques; cold trapping, radio-gas analysis and tritium transmission electron microscopic autoradiography. The tracer tritium was doped to the specimen by cathodic charging in tritium water and the release characteristics during the temperature increase were analysed using cold trap and radio-gas analyser methods. The corresponding structural changes were examined by transmission electron microscopic tritium autoradiography(1).

Experimentals

Al-Li alloys of both bulk (10mmX10mmX1mm) and thin sheet (2.8mmX0.2mm) specimens alloys containing 0.24, 0.94, 2.42 and 3.1wt.% lithium were prepared by cold rolling, annealed at 773-823K for 36Ks and aged at 473K for 86.4Ks in argon at 1 atm. After the heat treatment, the specimen was thinned electrolytically in a solution of nitric acid and methyl alcohol 1:3 volume ratio at 248K. After thinning the specimen was washed thoroughly with ethanol and tritium was introduced by cathodic charging as shown in figure 1. The tritium concentration in the 0.002N-sodium hydroxide was 1.86×10^-6 ppm. The specific radioactivity of tritium was 0.14mCi/cm^2. Both the bulk and thin foil specimens were charged at the current density of 0.05-5μA/cm^2 for 7.2Ks. Hydrogen analysed by the following three methods.

(1) Cold Trap Method

As shown in Figure 2, a constant helium gas flow was maintained while the bulk specimen was held in an electric furnace at temperatures from room to 973K for 30 minutes. The hydrogen trapping equipment was cooled with dry-ice. The released tritium gas passes through copper oxide(0.6X5mm) kept at 973K, and turns to tritium water by the reaction 3H_2+CuO→3H_2O+Cu.

The tritium water precipitates in a fine spiral copper pipe kept at dry ice temperature. The trapped tritium was rinsed out thoroughly by ACS-11 scintillator of volume 10cc and the radioactivity was measured by a liquid scintillation counter (Parkard TRI-CARB-3255).

(2) Radio-gas Analysis

Radio-gas analyser as shown in figure 3 uses a constant flow of dry helium and propane gas. A bulk specimen charged with tritium was held in an electric furnace and the specimen temperature was raised slowly from room temperature up to 1073K. The release characteristics of the absorbed tritium gas were measured by a five proportional counter tube set in parallel configuration.

The concentration of released tritium (R) was calculated by the following equation

\[ R = C_t \cdot \frac{1}{\eta} \cdot \frac{V}{V} \]  (1)
where $C_*, \gamma, v, V$ values are total counting rates of the released tritium, counting efficiency, gas flow rate (ml/min) and the volume of the proportional counter tube (30mlX5=150ml), respectively.

(3) Transmission Electron Microscopic Tritium Autoradiography

After electrolytical charging of tritium a sheet thin foil of Al-Li alloys was held at room temperature for three days to measure trapped tritium in a thin foil specimen. The specimen foil was covered with a collodion foil of about 10nm in thickness by dipping the foil into the solution. After drying, under a safety red light in a dark room, the surfaces of a thin foil specimen were coated with liquid photographic emulsion (Ilford L4) containing a monogranular layer of AgBr in the film. A loop method was used as shown in photo 1. After drying the emulsion, the coated specimen was held in an exposure vessel filled with high pure nitrogen at atmospheric pressure kept at 253K. The exposure time was 95-132 days. After the exposure, the composite was developed by Kodak 19, fixed, washed and was examined in a high voltage electron microscope JEM-1250. The whole process of the thin foil specimen preparation was described schematically in figure 4.

A tritium disintegrates to a stable helium atom by emitting $\gamma$-ray with a half-life of 12.2 years. The maximum and mean energies of the $\gamma$-ray are 18.6KeV and 6KeV respectively (3)(4). The corresponding maximum mean free paths in a Al-Li alloy and the emulsion film are 2.5μm (5). The mean free path in the silver bromide of fresh nuclear liquid emulsion (Ilford L4) was about 0.12μm (6).

Results

The tritium gas release characteristics in Al-Li alloys were measured as shown in figure 5 and 6 during increase in the temperatures by both cold trapping and radio-gas analysis. The Al-3.1wt.% alloy was annealed at 773K for 3.6Ks and aged at 473K for 86.4Ks. Electric current density of the specimen during tritium charging was $\sim$/cm$^2$ for 7.2Ks. A broad peak was detected in both figures in the range of 373-723K. This peak corresponds to the precipitation of $\psi$(AlLi) and $\phi'(Al_3 Li)$. During the release increase, a counting peak was seen in the vicinity of 873-973K as shown in figures 5 and 6. The counting peak is explained by the hydride formation inside the specimen.

The tritium concentrations in figures 5 and 6 were calculated using equation (1) by the radio-gas analysis. Similarly, in case of cold trapping method, the total tritium release as calculated by integrating the counting rates. The release values of cold trapping method and radio-gas analysis were 104.11ppm, 88.71ppm respectively. The agreement is fair. Transmission electron micrographs of Al-3.1wt.%Li alloy were shown in Photo 2 and 3. The specimen was annealed at 823K for 3.6Ks and aged at 473K for 86.4Ks. Precipitate of $\phi$(Al-Li) phase (7-9) in the grain boundary and $\phi'(Al_3 Li)$ phase (10-12) in the matrix were noticed. The tritium transmission electron microscopic autoradiography showed that the preferential trapping sites of hydrogen are $\phi'$ precipitates rather than $\phi$ precipitates as shown in Photo 4.

Conclusion

Both cold trapping and radio-gas analysis techniques were successful in showing hydrogen behavior in present Al-Li alloys. Hydrogen trapping was observed at precipitates $\psi$ and $\phi'$ of the Al-Li alloy. The microstructural hydrogen analysis showed that the transmission electron microscopic tritium autoradiography method is shown useful to examine the behavior of hydrogen in the present specimens.

References

3) Isotopes-pocket Book, the Isotopes Society, Japan, 1980.

Fig. 1 Tritium charging apparatus.

Fig. 2 Cold trap analysis of tritium release.
Fig. 3 Radio-gas analysis of the tritium release.

Photo 1 Loop method to apply liquid photographic emulsion to the specimen.

Fig. 4 Experimental procedure of tritium transmission electron microscopic autoradiography.
Fig. 5 Tritium release during increase in the specimen temperature analysed by cold trapping method.

Fig. 6 Tritium release during increase in the specimen temperature measured by radio-gas analysis in an Al-Li alloy containing 3.1 wt.% Li.

Photo 2 The precipitation of δ along the grain boundary.
Photo 3 Transmission electron microscopy of precipitates in an Al-3.1wt.%Li alloy.

Photo 4 Hydrogen trapping sites analysed by tritium transmission electron microscopic autoradiography.