Journal of Alloys and Compounds, *176* (1991) 7–12
JAL 0006

Hydriding of an industrial Al–2.7wt.%Li–Cu–Mg–Zr alloy

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(Received January 22, 1991)

Abstract

The absorption and desorption of hydrogen by Al–Li alloys were investigated by thermogravimetry in the pressure range 0.1–3.0 MPa and the temperature range 150–350 °C. The kinetic results complemented by microscopic observations of cross-sections show evidence of the formation, as a precipitate in the aluminium matrix, of a defined compound which turns out to be lithium hydride. The formation was controlled by the diffusion process in spherical symmetry. The pressure and temperature dependences were established.

1. Introduction

Al–Li alloys were first prepared in Germany in 1924; however, it was only in 1958 that Al–Li was used for wing panels in the U.S. Navy's Vigilante aircraft and then abandoned after number 177 as a consequence of poor ductility and fracture toughness. Nowadays, because of both economic and technical considerations, these alloys are again being considered as promising materials for aircraft and space applications. Consequently, the determination of their mechanical properties and corrosion resistance is the subject of intensive investigations. The particular role played by hydrogen absorption in changes in ductility, fracture toughness and corrosion resistance is of basic interest. It is known that the 7000 and 2000 series aluminium alloys are very sensitive to hydrogen embrittlement; in addition, Al–Li alloys absorb hydrogen more easily and desorb it with more difficulty than conventional aluminium alloys [1].

Quantitative data on the hydrogen solubility, diffusion and permeability of aluminium alloys are not numerous [2]. According to Eichenauer *et al.* [3], the atomic hydrogen solubility is very low (10^{-4} ppm 400 °C). Bastien and Azou [4] give a hydrogen diffusion coefficient in aluminium of $D_H = 10^{-12}$–10^{-9} cm^2 s^{-1} at room temperature and Nakashima *et al.* [5] show that the hydrogen diffusion coefficient decreases with increasing lithium content. Experiments on hydrogen charging of Al–Li (8090) solid samples were carried out by electrolysis in melted salts at a temperature of 190 °C for durations of 10–30 h; a maximum quantity of inserted hydrogen of 60 ppm was found [7]. Tests of hydrogen absorption on Al–Li disks were

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performed with hydrogen gas at a pressure of 40 MPa and a temperature of 190 °C for 20 h. According to the data published [7], it seems that hydrogen charging by gaseous hydrogen is unsuccessful. Ozouf-Binfeld [7] underlines the role played by the physical and chemical state of the surface on the reproducibility of hydrogen absorption, *i.e.*, the level of cold working, the thickness of the oxide layer, lithium surface segregation and lithium hydroxide formation, the trapping of hydrogen molecules and the possible pollution of hydrogen by oxygen molecules.

2. Experimental conditions

The experiments were carried out by thermogravimetry in a high pressure microbalance with a limiting sensitivity of 2 μg. The device was equipped with a turbomolecular pump which allowed a vacuum of 2×10^{-4} Pa free of oil.

The sample consisted of 200 mg of chips, filed in an ingot, with an average size of 200 μm. The sample was placed on a silica holder. The hydrogen used was of "U" quality of "Air Liquide" and was cleaned free of oxygen and water vapour traces by successively passing it through firstly molecular sieves and secondly copper chips which were heated to a temperature of 400 °C.

Since the Al–Li alloys appeared to be very sensitive to poisoning by substances which are gassed out from the stainless steel walls of the laboratory tubes, *i.e.* oxygen and carbon monoxide, the following process was adopted. For formations the device was placed in a vacuum (2×10^{-4} Pa), filled with hydrogen at the given pressure and then heated to the determined temperature. For decompositions (after a formation) the device was cooled under hydrogen pressure, then evacuated at 2×10^{-4} Pa and heated to the chosen temperature.

3. Experimental results

3.1. First formations

We "generally" easily obtained the first formation, *i.e.* the hydridation of the sample, in a range of temperatures varying from 150 to 400 °C and pressures from 0.1 to 3 MPa. In fact, a long series of experiments had been developed with a satisfying reproducibility when we were faced with the impossibility of reproducing the preceding experiments even though nothing had apparently changed in the protocol. After a long series of tests, successful experiments were obtained again when the sample (after being filed) was placed for 24 h in a sealed vessel containing a saturated water vapour atmosphere.

3.2. Formations on the alloy 8090

(T 351; Al–2.7wt.%Li–1.3wt.%Cu–1.1wt.%Mg–0.09wt.%Zr, cold working 4.5%, annealed for 12 h at 135 °C)

In the following data the hydrogen uptake is expressed as a mass change ratio which is calculated by assuming that magnesium forms MgH_2, zirconium forms ZrH_2 and lithium forms LiH. With a sample mass of 100 mg the stoichiometric hydrogen uptake is 0.4787 mg, which leads to a maximum mass change ratio of 0.4784%. This result is equivalent to a transform fraction $\alpha = 1$.

In Fig. 1 a series of curves of hydrogen uptake *vs.* time at a given pressure of 3 MPa and temperatures ranging from 149 to 343 °C is displayed. The following can be noted.

Firstly, there is a change from pseudosigmoidic curves at low temperatures to continuously speed-decreasing curves after 184 °C. These latter curves become linear and can be expressed by the equation

$$[1-(1-\alpha)^{1/3}]^2 = Kt$$

This equation, according to Jander [8], represents a diffusion-controlled reaction in a sphere.

Secondly, hydridation is quite fast at 343 °C: 80% of the reaction is completed in 2 h and the maximum hydrogen uptake is 0.578%, which corresponds to 120% of the calculated value. These data show that additional hydrogen is fixed in the form of aluminium hydride or more probably as trapped hydrogen atoms in structural defects.

3.3. Pressure and temperature dependences

The effect of temperature on the initial reaction rate was determined from the slope of the curves $H\% = f(t)$ at their origin. The reaction rates show a linear dependence on temperature for both families of curves.

For the pressure dependence it appears that for $P_{H_2} < 1$ MPa the initial reaction rate V_0 *vs.* P_{H_2} is correctly expressed by the relation $V_o = f(P_{H_2})^2$,

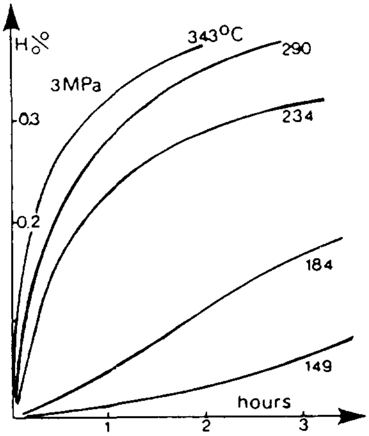

Fig. 1. First formation curves: mass of hydrogen fixed *vs.* time; $P_{H_2} = 3$ MPa, temperatures ranging from 149 to 343 °C.

whereas for pressures above 1 MPa there is a linear dependence of V_0 *vs.* P_{H_2}.

3.4. Reversible formation–decomposition

This study was carried out on the alloy T351 (Al–2.3wt.%Li–0.1wt.%Zr, cold working 2.5%, annealed 12 h at 135 °C).

After a first formation under conditions of 3 MPa and 350 °C, the substance can be "partially" decomposed under a temperature of 350 °C and a vacuum of 2×10^{-4} Pa. This decomposed fraction, which represents approximately 65% of the first formation, can be reformed reversibly. The formation curves become linear and can be expressed by the equation

$$1-(1-\alpha)^{1/3}=Kt$$

where α is the transformed fraction, t is time, K is a constant. This equation represents a phase-boundary-controlled reaction in spherical symmetry.

The following can be noted.

Firstly, the reaction rate increases from one formation to the next; by cycling under the same conditions, an activation process occurs during the three first formations, to reach a constant value thereafter.

Secondly, these formations are carried out under very low pressures relative to the pressure required for the first formation. Undoubtedly there is an activation of the surface, *i.e.*, dissociation sites, cracks, etc, between the first and second formations, as is often the case with hydride-forming systems.

If the initial reaction rate V_0 is plotted *vs.* the hydrogen pressure, for pressures ranging from 0.154 to 0.6 MPa there is a linear relationship between $\ln V_0$ and $\ln P_{H_2}$. For pressures higher than 0.6 MPa V_0 seems to be independent of P_{H_2}.

3.5. Morphological observations

Microscopic observations were carried out on powder samples before a formation, after a formation and after decompositions. The powder was embedded in a resin which was polished to give cross-sections of the grains. The finishing operation consisted of polishing with a 3 μm diamond spray and the "OPS" polishing liquid of "Struers". The samples were then washed with ethyl alcohol and observed at magnifications of ×400 and ×800.

Figure 2 shows the unreacted sample. Figure 3 represents a cross-section of a grain after hydridation. An abundant precipitate with a concentration of particles near the surface and larger particles near the centre of the grain can be observed. This precipitate exhibits several shapes, long prismatic needles and flat hexagonal or triangular tablets, in agreement with observations of Dickenson *et al.* [9]. All forms can be related to the cubic system.

Figure 4 shows a sample after decomposition. The main results are the disappearance of the abundant precipitate located near the outside of the grain and the persistence of some of the large central precipitates. This last point explains the difference in composition which is observed between the

Fig. 2. Al–Li alloy before hydridation.

Fig. 3. After H_2 reaction an abundant LiH precipitate with well-defined crystallographic particles is present; a concentration of particles near the surface and larger particles near the centre of the grain can be observed.

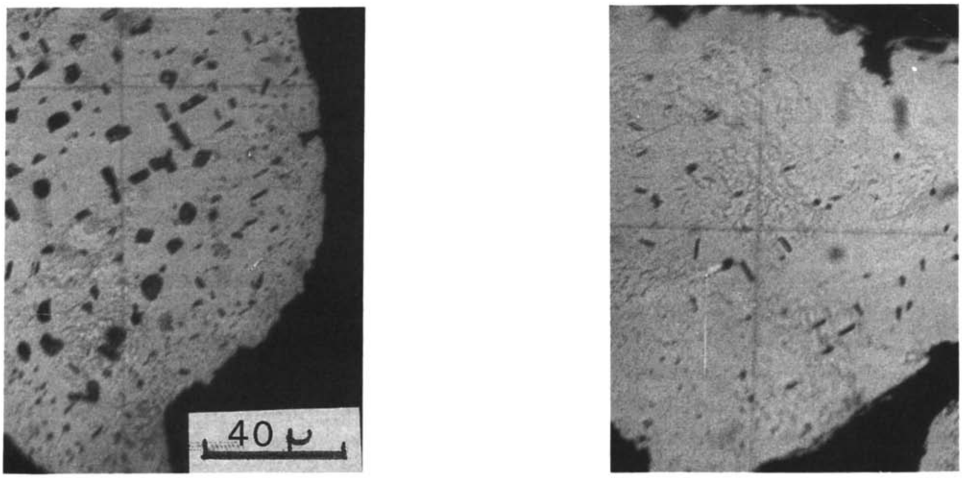

Fig. 4. After decomposition the near-surface precipitate is decomposed but some of the large central particles remain.

first formation and the subsequent ones. These large central particles are not decomposed but probably play a role in the easier subsequent formations.

3.6. Identification of the precipitate in Al–Li alloys

A similar precipitate to that shown in Fig. 3 has been previously described in an Al–Li–Cu–Mg (CP 276) alloy and attributed to porosity from welding [10]. Dickenson *et al.* [9, 11] also observed severe porosity after wet air annealing of Al–3wt.%Li and as well as LiH particles they noted crystallographic regularity and alignment along grain boundaries of some particles. They were the first authors to give evidence of LiH precipitation in an Al–Li alloy. In a test of secondary ion mass spectrometry applications related to hydrogen localization, Outrequin *et al.* [12] obtained on our sample their Fig. 4, in which "the Li image is the negative of the $^{27}Al^+$ picture and the lateral distribution of hydrogen corresponds nicely to the lithium one". This result gives evidence of LiH precipitation.

4. Conclusions

The first hydridation of Al–Li alloys by gaseous hydrogen requires a hydrogen pressure and temperature and an attack of freshly prepared surface by water vapour. Under these conditions H_2 molecules can be dissociated and the reaction is controlled by diffusion in a sphere. The result is the formation of a cubic LiH precipitate which can be partially under vacuum.

Acknowledgment

We thank Dr. Habashi from Ecole Centrale des Arts et Manufactures (Chatenay Malabry, France) for providing us with samples of Al–Li alloys and for constructive discussions on H/Al–Li behaviour.

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