



A study of hydrogen permeation in aluminum alloy treated by various oxidation processes

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Abstract

A set of oxide coatings was formed on the surface of an Al alloy (wt%: Fe, 0.24; Si, 1.16; Cu, 0.05–0.2; Zn, 0.1; Al, residual) by means of various oxidation processes. The hydrogen permeability through the aluminum alloy and its coating materials was determined by a vapor phase permeation technique at temperatures ranging from 400 to 500°C using high-purity H₂ (99.9999%) gas with an upstream hydrogen pressure of 10⁴–10⁵ Pa. The experimental results show that the hydrogen permeability through aluminum oxide coating is 100–2000 times lower than that through the aluminum alloy substrate. This means that the aluminum oxide is a significant hydrogen permeation barrier. A high hydrogen permeation resistance was observed in an oxide layer prefilmed in 200°C water, while an anodized aluminum oxide film had a less obstructive effect, possibly caused by the porous structure of the anodic oxide. The hydrogen permeability through films of aluminum oxide was not a simple function of the aluminum-oxide phase configuration. © 1997 Elsevier Science B.V.

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1. Introduction

For fusion-reactor-concept design work, tritium permeation is one of the most important questions to consider. The transport characteristics of hydrogen isotopes, deuterium and tritium, governed by the thermodynamics of the structure materials, are of great reference value in recycling fuel particles, controlling plasma density in the reactor core and estimating the quantity of tritium introduced and lost during the operation of the reactor. Some of the principal metals considered for structure application are W, Mo, Cr, Fe and Al [1]. There are limitations for the use of these metals as reactor components in critical environments. Therefore some ceramic films have been studied in order to make up for the deficiencies of metals in such applications.

One of the properties that needs to be improved is a

reduced tritium permeation rate. There are two ways to produce a tritium permeation barrier. One is to form dense oxide films on the surface with the metals themselves. The other is to prepare a surface coating, such as TiN, TiC, SiC, Al₂O₃ [2], Cr₂O₃ [3] and TiN + TiC composite film [4] by PVD (physical vapor deposition) or CVD (chemical vapor deposition).

Considering cost and safety, hydrogen is often used to simulate diffusion properties of tritium because of their similar chemical nature. In order to determine the most effective oxidation method and the oxide phase that is most effective in decreasing the hydrogen permeation rate, we carried out a study of hydrogen permeation in aluminum alloys treated by various oxidation processes.

2. Experimental procedure

The Al alloy had a composition in wt% of: Fe, 0.24; Si, 0.16; Cu, 0.05–0.2; Zn, 0.1; Al, residual. The specimens were circular disks with a diameter of 20 mm and thick-

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Table 1
Oxidation processes and resulting oxide film thicknesses

Sample	Film thickness (μm)	Oxidation process	Surface color
Al alloy with native oxide			
M	12.6 + 25.0 ^a	anodization + $\text{K}_2\text{Cr}_2\text{O}_7$ sealing	silvery white
P	7.1 + 18.4 ^a	anodization + water sealing	golden
L	12.4 + 31.9 ^a	anodization + amino-triethanol sealing	silvery white
A	4.4 + 4.4	boiling amino-triethanol	greyish white
H	4.3 + 4.3	boiling $\text{Na}_2\text{Cr}_2\text{O}_7$	silvery white
D	3.9 + 3.9	200°C water prefilming	snowy white
K	2.7 + 2.7	100°C water prefilming	snowy white

^a The film thickness of the anodic oxide facing the cathode is different from that of the opposite side.

ness of 0.8 mm. Various oxidation treatments were applied to produce oxide coating on the surface of the Al alloy. The thickness of the oxide film was determined by observing cross-sections of the specimens by SEM (scanning electron microscope). Table 1 lists the details of the pre-filming process, film thickness and surface appearance of each specimen. The oxide samples were subject to corrosion by exposure to soft water of pH nearly equal to 6.0 for several weeks. The structure of the samples of both before-corrosion and after-corrosion was identified with X-ray diffraction taken from the surface of the samples using $\text{Cu K}\alpha$ radiation with a Philips PW1700 diffractometer.

A permeation apparatus that is mainly made of stainless steel with a based pressure less than 10^{-6} Pa was divided by a specimen disk into an upstream (hydrogen supply) side and downstream side. High-purity hydrogen (99.9999%) was supplied to the upstream side passing

through a liquid nitrogen cooled pipeline which was used to trap impurities. The hydrogen pressure at the upstream side was maintained stationary between 10^4 – 10^5 Pa by controlling the gas supply quantity. The pressure downside is a linear function of hydrogen flow rate which was calibrated against a standard leak. Therefore, it was possible to measure the hydrogen permeation quantitatively by this dynamic procedure. The Al alloy specimens with oxide coating were kept at a constant temperature ranging from 400 to 500°C. Hydrogen permeating to the downside was analyzed by a BA (Bayard–Alpert) gauge. The details of the apparatus are shown schematically in Fig. 1.

3. Results and discussion

Aluminum is a reactive metal according to thermodynamics. In dry oxygen, a thin compact film of aluminum

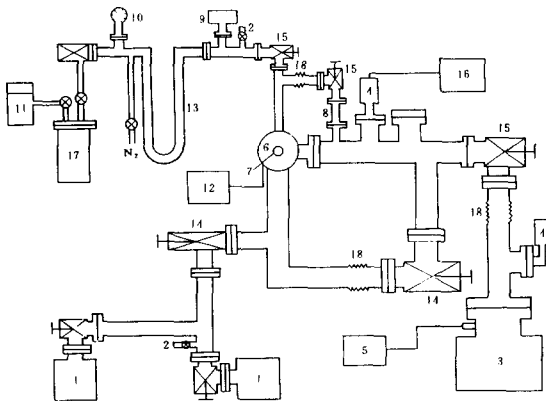


Fig. 1. A schematic diagram of hydrogen permeation apparatus. (1) Sorption pump; (2) air bleeder; (3) ion pump; (4) BA gauge; (5) power of ion pump; (6) resistance furnace; (7) specimen disk; (8) standard leak; (9) vacuum gauge; (10) gas manometer; (11) hydrogen generator; (12) temperature control system; (13) liquid nitrogen cooled pipeline; (14) metal UH vacuum valve; (15) fluororubber UH vacuum valve; (16) UH vacuum piezometer; (17) hydrogen storage and (18) bellows.

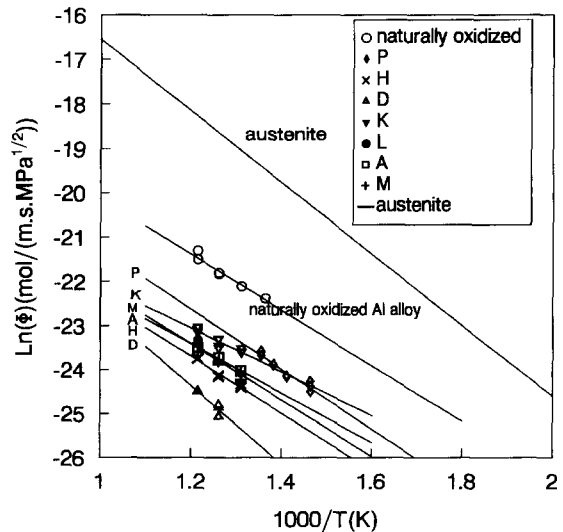


Fig. 2. Temperature dependence of hydrogen permeability for Al alloys treated by oxidation processes. Literature data of austenitic steel [4] is also shown for comparison.

Table 4
Experimental conditions and permeation parameters obtained from fitting H permeability data from Fig. 2

Sample	Temperature (°C)	Φ_0 (mol/m s MPa ^{1/2})	E_ϕ (kJ/mol)	Permeation resistance ratio of oxide/substrate
Naturally oxidized Al alloy	460–550	1.00×10^{-6}	52.5	
D	520–550	1.22×10^{-6}	74.5	> 2000
H	490–550	1.26×10^{-7}	54.1	800
K	490–550	3.83×10^{-8}	41.4	600
A	490–550	5.93×10^{-8}	46.8	540
M	490–550	1.53×10^{-7}	53.4	140
P	410–465	5.37×10^{-7}	56.7	80
L	520–550			150

oxide with a limiting thickness of about 3 nm grows. Film thickness increases in the presence of water vapor. At room temperature and 100% relative humidity, about twice as much oxide is formed as in dry oxygen. A duplex film generally forms in wet environments; the continuous oxide layer closest to the metal surface changes to hydroxylated film at the solid–gas interface [5–7].

In this experiment, X-ray diffraction analyses indicated that the film on the surface of Al alloy samples was not simply composed of aluminum oxide. The hydroxylated phase consisted of crystalline and amorphous phases. The phase ratio of various compounds in the film depended on the oxidation treatment of each Al alloy specimen. The mixture ratios of oxide phase for all the oxidation processes are presented in Table 2.

Using the measured values for the hydrogen permeation rate, J , at steady state, the hydrogen permeability, Φ , at a given temperature and driving pressure was calculated according to

$$\Phi = \frac{JL}{ASQRT P}, \quad (1)$$

where L and A are sample thickness and surface area, respectively, and P is the hydrogen pressure on the upstream side. The permeability, Φ , of each sample at several temperatures is listed in Table 3.

It is clearly seen in Table 3 that the permeability parameters of the artificially oxidized Al alloys are from 4 to 20 times lower than those of Al alloy with native oxides. With respect to accuracy, the decreasing extent of hydrogen flow due to oxide coating should be compared to Al alloy substrate itself. That means that the native oxide layer must be removed from the reference sample. Then the cleaned surface should be coated with hydrogen permeable Pd film. Since we are more concerned about relative permeation resistance contributions of films and because the thicknesses of the oxides were rather thin, Al alloys with native oxides were selected as reference samples. The permeation data for the metal substrate refers to the native oxide specimen.

Fig. 2 shows the permeability as a function of the reciprocal temperature, $\ln \Phi$ versus T^{-1} . The experimental

data of the apparent permeability for each sample were fitted according to the Arrhenius law. A permeation resistance parameter, k , was defined to present the reduction factor of hydrogen flow attributed to oxide film:

$$k = \left(\frac{J_m}{J_f} - 1 \right) \frac{L_m}{L_f}, \quad (2)$$

where J_m and J_f are hydrogen flow rates through the samples with and without an artificial oxide film and L_m and L_f the thickness of Al alloy substrate and oxide layer. The physical meaning of parameter k is the ratio of hydrogen flow rate through the metal substrate to that through a similar thick oxide layer for a fixed temperature and upstream hydrogen pressure. In other words, it is the ratio of permeation resistance ability for the oxide layer and metal substrate. Table 4 presents the fitting data of the permeation coefficients derived using the Arrhenius equation and the permeation resistance ratio of the oxide film to the Al alloy substrate.

The permeability of the samples treated by various oxidation processes decreased by nearly one order of magnitude, which suggests that aluminum oxide/hydroxide, whether crystalline or amorphous, had an appreciable hydrogen permeation resistance effect. The sample pre-filmed in 200°C water served as a good hydrogen permeation barrier. On the contrary, the samples with anodic coatings had little effect in preventing hydrogen diffusion. This can possibly be explained by the porous structure of anodic aluminum oxides and this in spite of these films being sealed in subsequent treatments. Further work should be done to find the intrinsic relation between the magnitude of hydrogen permeability and phase components as well as the structure of the oxide layers formed by the various oxidation techniques.

References

- [1] K. Watanabe et al., *J. Vac. Sci. Technol.* 5 (1987) 237.
- [2] S. Tominett, M. Caorlin, J. Campasilvan, A. Perujo, F. Reiter, *J. Nucl. Mater.* 176&177 (1990) 672.

- [3] D. Baiquan, H. Qirong, D. Jiaju et al., *Fusion Plasma Phys.* 14 (4) (1994) 39, (in Chinese).
- [4] S. Changqi, *China Nuclear Science and Technology Report*, Aug. 1992, p. 11.
- [5] J.E. Hatch, *Aluminum: Properties and Physical Metallurgy* (American Society for Metals, Metals Park, OH, May 1984) p. 17.
- [6] J.E. Hatch, *Aluminum: Properties and Physical Metallurgy* (American Society for Metals, Metals Park, OH, May 1984) p. 242.
- [7] J.E. Hatch, *Aluminum: Properties and Physical Metallurgy* (American Society for Metals, Metals Park, OH, May 1984) p. 309.