

Hydrogen-straining effects in Al

E. Lunarska^{a,*}, O. Chernyayeva^a, L. Spivak^b

^a Institute of Physical Chemistry of the Polish Academy of Science, 01-224 Warsaw, ul. Kasprzaka 44/52, Poland

^b Perm State University, Perm, Russia

Received 13 July 2004; received in revised form 15 February 2005; accepted 21 February 2005

Available online 14 July 2005

Abstract

The formation of the transition hydrogen permeation minimum and maximum upon the application and cessation of cathodic polarization of Al in 0.01N NaOH has been accounted for the strain induced hydrogen uphill diffusion. The straining of Al due to the cathodic polarization has been confirmed by the effect of cathodic polarization on the stress–strain and creep relationships and on the Al elastic modulus evaluated by means of the internal friction measurements. The role of the Al hydride formation has been discussed.

© 2005 Elsevier B.V. All rights reserved.

Keywords: Al; Cathodic polarization; Hydrogen permeation; Strain relaxation

1. Introduction

At metal straining, the solute atoms move to the extended regions [1] and it results in the strain relaxation [2]. The hydrogen permeation affected by the uphill diffusion originated from the strain imposed by the entering hydrogen atoms has been observed [3] and analysed [4] for Pd and its alloys. In the course of the electrochemical measurements of hydrogen permeation [5] through Al [6] and its alloy [7] the formation of transition hydrogen permeation minimum and maximum has been observed upon the application and the cessation of the cathodic polarization (Fig. 1). Previously carried out analysis of these phenomena [6] allowed attribute the effect to the complex hydrogen transport within the membrane due to the metal straining. It could be expected that imposing the strain at cathodic polarization should also affect the elastic and plastic properties of Al. This was studied in the presented work.

2. Experimental procedure

Electrochemical hydrogen permeation measurements [5] were carried out in 0.01N NaOH for Al membranes (0.0025–

0.2 cm thick) using the double cell. The anodic current (J), being the measure of hydrogen permeation rate through the membrane, was recorded in the egress cell at the open circuit potential, at application (permeation build up) and at cessation (permeation decay) of cathodic polarization in the ingress cell. The increased cathodic polarization ($i_c = 20\text{--}120 \text{ mA/cm}^2$) was applied step by step (“on–on” mode) or with intermediate cessation between the each step (“on–off” mode). The effect of cathodic polarization on tensile strains (ϵ), torsion creep deformation (γ) and shear modulus (G) of Al was evaluated in the following tests, respectively:

- tensile stretching (specimens, 0.017 cm thick) with the strain rate $2\text{--}5 \times 10^{-4} \text{ s}^{-1}$;
- torsion creep of wires (cross-section, 1 mm \times 1 mm) initially twisted in inversed torsion pendulum within the elastic region (shear stress, $\tau = 30 \text{ MPa}$);
- torsion oscillation (frequency, $f = 1.5 \text{ Hz}$) of wires.

3. Results and discussion

At application of both modes of cathodic polarization, the minimum of permeation current decreased with the increase in polarization (Fig. 2) while in the case of “on–on” mode

* Corresponding author. Tel.: +48 22 632 32 21; fax: +48 22 632 52 76.
E-mail address: ellina@ichf.edu.pl (E. Lunarska).

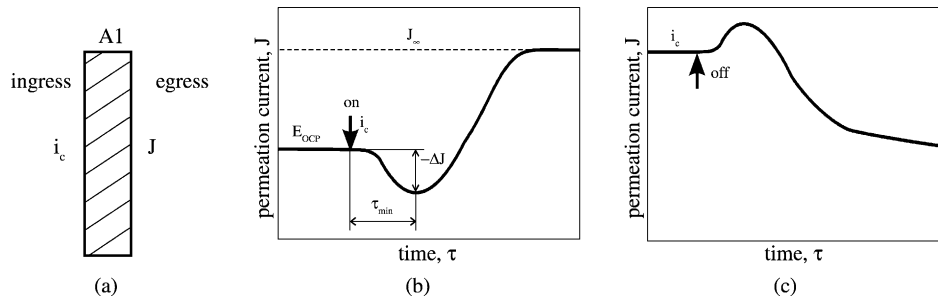


Fig. 1. Setting of double cell experiment (a) and the examples of buildup (b) and decay (c) of hydrogen transient permeation recorded in the egress cell at (b) application (↓on) and at (c) cessation (↑off) of cathodic polarization in the ingress cell, respectively.

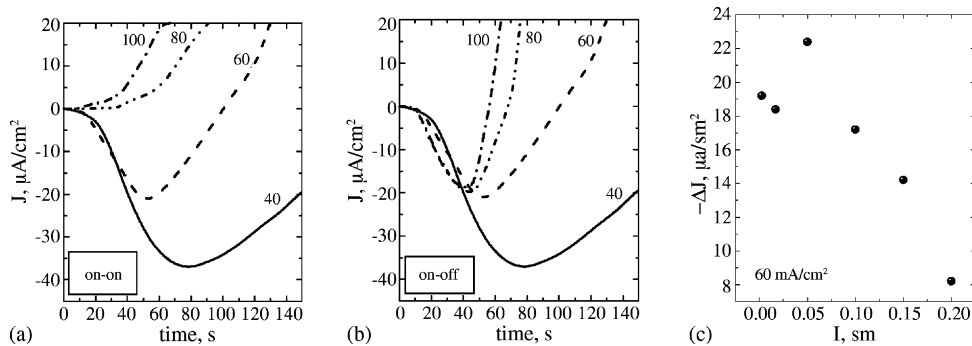


Fig. 2. The appearance of the hydrogen permeation minimum at application of increased cathodic polarization according to “on–on” (a) and “on–off” (b) modes and the effect of the membrane thickness on the depth of permeation minimum (c).

it vanished at high polarization (Fig. 2a). The permeation minimum increased also with the increased thickness of the membrane, cf. Fig. 2c. Cathodic polarization of tensile tested specimen resulted in the decrease in the strain without change or even with decrease in the stress (Fig. 3). Similarly as in the case of hydrogen permeation measurements (Fig. 2a and b), the effect of increased polarization was more pronounced in the “on–off” (Fig. 3a) than in the “on–on” mode (Fig. 3b). The change of the slope of the stress–strain curve, and thus the change of the strain hardening rate due to the cathodic polarization can also be seen.

Application of cathodic polarization produced the creep deformation of wires, as recorded in torsion test (Fig. 4a). At cathodic polarization, the shear modulus (Fig. 4b) has been also decreased, as established in the oscillation test. Some recovery of above parameters can be seen after the cessation of polarization (Fig. 4b).

As follows from the obtained data, the straining of Al at the application of cathodic polarization is significant and can be considered at the discussion of the origin of the unusual hydrogen permeation. The diminishing of the effect with the increase in the membrane thickness

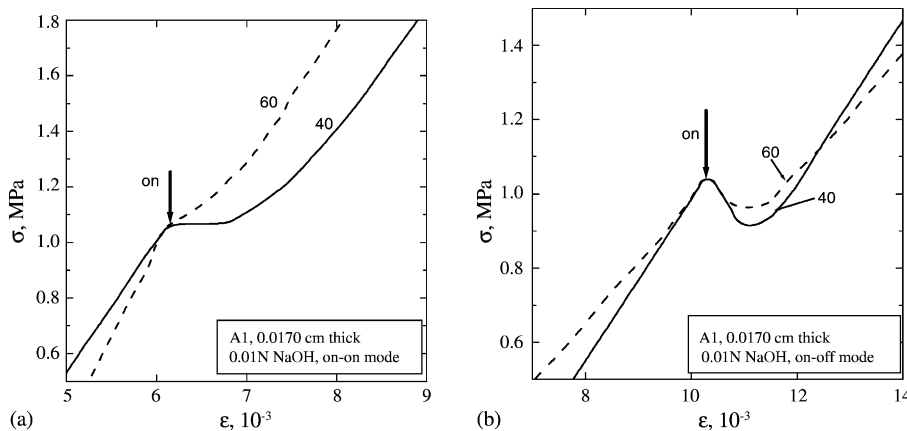


Fig. 3. Effect of application of cathodic polarization according to “on–on” (a) and “on–off” (b) modes on the appearance of the stress–strain curve of the tensile tested specimens.

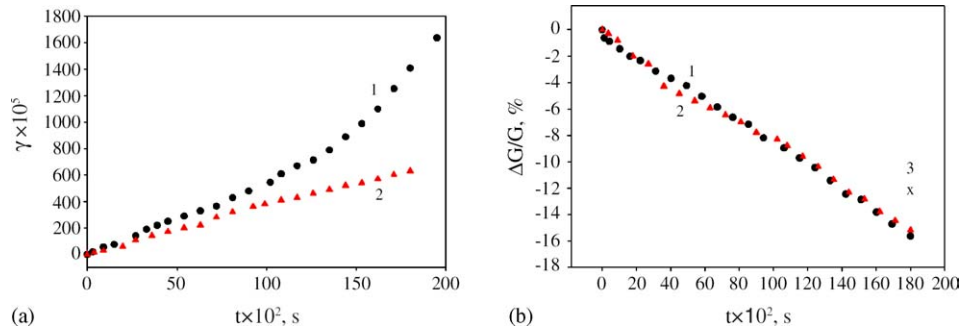


Fig. 4. Effect of cathodic polarization on the creep deformation (a) and on the change of the elastic modulus (b) of Al established in torsion tests. (1, 2) Different electrochemical parameters, (3) data obtained after the cessation of cathodic polarization.

(Fig. 2c) suggested that the near surface processes have been involved.

The metal straining at the ingress surface of the membrane at cathodic polarization may be caused by the hydrogen atoms entering the metal lattice or by the formation of the solid phase surface layer. Because of the very low hydrogen solubility in Al (about 10^{-8} at/at [8]) the strain imposed by the entering hydrogen (about 6×10^{-10}) cannot be sufficient to produce the observed effects. Therefore, the formation of the solid phase surface layer should be taken into account. The symmetry in the build up and the decay hydrogen permeation transients (Fig. 1) demands the reversibility in the processes occurring within the surface layer at application and at cessation of cathodic polarization. Although the surface Al_2O_3 layer imposes the stresses in aluminium [9] it is formed at anodic not at cathodic polarization [9] and once formed it cannot be removed by cathodic polarization [10]. Therefore, the oxide layer cannot provide the observed reversibility of the effect.

At cathodic polarization in alkaline solution, Al hydride is the stable form [11]. Because of the difference of the lattice structure and lattice parameters of metal and hydride, creation of the stresses high enough to overcome the yield stress can be expected in the metal at the formation of hydride. At

cessation of cathodic polarization, the hydride is unstable and transforms to the amorphous hydroxide [11]. This causes the relaxation of stresses. Formation and decomposition of the Al hydride can be accounted for the reversibility and symmetry of the observed effects.

At increased polarization the imposed elastic strain approaches the yield limit and no further increase in stress occurs because of the plastic deformation of metal (Fig. 5a). This is accompanied by the increase in dislocation density [12]. Therefore, the increase in the elastic strain and stress is limited, whereas amount of entering hydrogen still increases with the increasing polarization. As a result, at the certain polarization, the inward hydrogen flux originated from the gradient of hydrogen concentration overcomes and suppresses the outward one originated from the strain gradient, and no permeation minimum would be observed, cf. Fig. 2 a. After cessation of cathodic polarization causing the plastic deformation, some residual stress and the change in the metal structure remain (Fig. 5b). In the “on–off” mode, the relaxation of the surface layer at cessation of polarization allows the developing the effect at the application of the next, higher polarization (Fig. 2b). In the case of “on–on” mode, no relaxation occurs between the application of increased cathodic polarization and still more and more pronounced

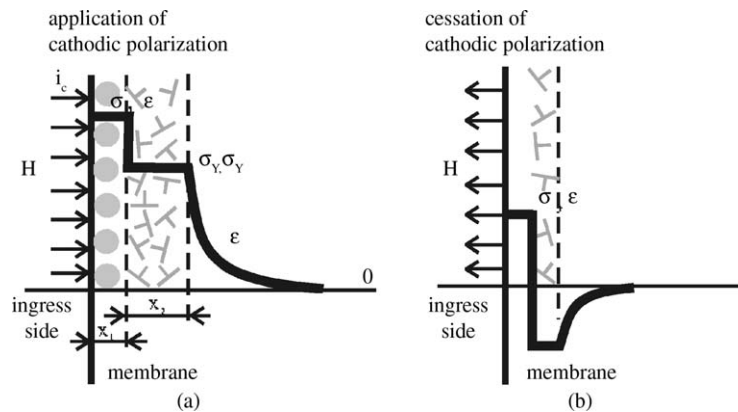


Fig. 5. Schematic presentation of the stress and strain state within the surface layer at the ingress side of the membrane at application of cathodic polarization (a) causing the overcoming the yield limit (σ_Y) and at cessation of that cathodic polarization (b). X_1 , surface layers exhibiting the hydride deformation of metal lattice; X_2 , the plastically deformed zone.

change of the structure of surface layer hinders the effect (Fig. 2a).

Although the above assumption on the formation and decomposition of the hydride phase should be confirmed, for example by the special X-ray analysis, it could be indirectly supported by the data obtained in torsion tests. According to the strain and stress distribution in twisted specimen, the test is especially sensitive to sample the change of elastic and plastic properties of the surface layer. The observed increase in the creep deformation due to cathodic polarization has been quite similar to the effects of hydrides formed at cathodic hydrogen charging of Pd, V, Nb, Ta [13]. The observed decrease in the shear modulus can also justify the change of the structure of the near surface part of Al specimen, similarly as in the case of hydride forming metals.

4. Conclusions

1. Application of cathodic polarization in the alkaline solution to Al modifies the stress-state of the metal surface layer, and therefore, may cause the formation of the uphill hydrogen flux affecting the hydrogen permeation through the metal.
2. Formation of Al hydride, stable at cathodic polarization in alkaline solution might be considered as the origin of the metal straining, as follows from the similar effects of

cathodic polarization on the creep and elastic properties produced in Al and on those observed in other hydride forming metals. However, this assumption demands the further confirmations.

References

- [1] W.S. Gorsky, Phys. Z. der Sowjetunion 8 (1935) 451–471.
- [2] S. Konobeevsky, Zh. Eksperimentalnoji i Teoreticheskoi Fizyki 6 (1943) 200–214 (in Russian).
- [3] F.A. Lewis, J.P. Magennis, S.G. McKee, P.J.M. Ssebuwufu, Nature 306 (1983) 673–675.
- [4] B. Baranowski, S. Sieniutycz, P. Salomon (Eds.), Advances in Thermodynamics, Flow, Diffusion and Rate Processes, Taylor and Francis, NY, 1992, pp. 168–199.
- [5] V.M.A. Devanathan, Z. Stachurski, J. Electrochem. Soc. 111 (1964) 619–623.
- [6] E. Lunarska, T. Ryumshina, O. Chernyayeva, Izvestja RAN Seriya Fizicheskaya 67 (2003) 278–283.
- [7] M.J. Danielson, Corros. Sci. 44 (2002) 829–840.
- [8] G.M. Bond, I.M. Robertson, H.K. Birnbaum, Acta Met. 36 (1988) 2191–2197.
- [9] D.H. Bradhurst, J.S. Leach Llewelyn, J. Electrochem. Soc. 113 (1966) 1245–1249.
- [10] S.-M. Moon, S.-I. Pyun, Corros. Sci. 39 (1997) 399–408.
- [11] G.G. Perrault, J. Electrochem. Soc. 126 (1979) 199–204.
- [12] J.W. Watson, Y.Z. Shen, M. Meshii, Metall. Trans. 19A (1988) 2299–2305.
- [13] L. Spivak, N. Skryabina, M. Kac, Hydrogen and Mechanical Aftereffect in Metals and Alloys, Perm University Press, Perm, 1993, (in Russian).