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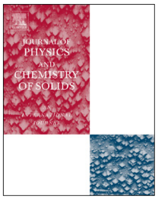

Studies on hydrogen diffusivity in iron aluminides using the Devanathan–Stachurski method

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ABSTRACT

An electrolytic method for cathodic hydrogen saturation developed by Devanathan and Stachurski was successfully used to study hydrogen diffusivity in iron aluminides. Both an appropriate electrolyte and a saturating current density are required for this method. A proper form of the saturation curve was only obtained with 35% NaCl electrolyte, which removed the oxide film blocking hydrogen penetration without further corrosive destruction of the iron aluminide. The optimum saturation current density for determining the most reliable diffusivity was 1.91 A/cm^2, yielding $D_{\mathrm{eff,H}} = 4.81 \times 10^{-6}$ cm^2/s for Fe–40 at.% Al.

1. Introduction

Iron aluminides belong to a group of high-temperature creep-resisting materials with unique physicochemical and mechanical properties that mean they are potential materials for applications in high-temperature and high-corrosion environments [1–3].

One of the main obstacles hindering application of these alloys is their low plasticity at room temperature, caused by hydrogen embrittlement among other factors [4]. Hydrogen originates as a result of Al reaction with moisture contained in the air and penetrates the iron aluminide lattice, causing a decrease in plasticity. Therefore, an understanding of the hydrogen transport process in Fe–Al alloys is an important research problem.

Although numerous techniques can be used to study the amount of hydrogen absorbed in metals and alloys, such as thermal convection, alloying, and vacuum extraction techniques, gas chromatography or ionic mass spectrometry and electrochemical methods are still often used, including the method developed in 1962 by Devanathan and Stachurski (DS) [5]. In this method, the entry side of a membrane made of the metal being studied is in contact with a electrolyte, from which hydrogen is released as a result of cathodic polarisation forced by an external current source. A large proportion of this hydrogen usually escapes from the solution, but some of it penetrates into the membrane and migrates to the exit side. To accelerate evolution from the membrane, hydrogen is subjected to electrochemical ionisation (oxidation) in an alkaline solution at a constant electrode potential on the membrane exit side [6]. The resulting ionisation current is a direct measure of the rate of hydrogen permeation through the membrane and can be analysed from the standpoint of hydrogen transport [7]. The membrane exit side is coated with a thin layer of palladium. This layer should: (1) prevent reaction of the metal with the alkaline solution (anodic passivation, which would involve an additional current flow and hence an apparent increase in the hydrogen permeation rate); and (2) accelerate electrochemical ionisation of hydrogen atoms and thus prevent their chemical desorption (which would correspond to an apparent reduction in the permeation rate). Electrochemical measurement of hydrogen diffusivity is both convenient and extremely accurate. A change in current density of 1×10^{-3} mA/m^2, which is easily measurable, corresponds to a change in the stream of permeating hydrogen of 1.04×10^{-8} mole H/m^{2}s [6].

The results obtained using this technique can better reflect actual conditions of high hydrogen activity than data obtained for the permeation of pure gaseous hydrogen at a low pressure. The DS method can be used to determine the effective hydrogen diffusion coefficient ($D_{\mathrm{eff,H}}$) and hydrogen solubility in a material [8,9]. Moreover, extension of this technique by measurement of the desorption rate on both sides of a metal membrane saturated with hydrogen can be used to determine the total hydrogen content by differentiating the amount of hydrogen diffusing from the estimated amount and the distribution of hydrogen trapped in the membrane [10]. Because of its high sensitivity and the possibility of measuring hydrogen diffusivity at low temperatures in a short time, the DS method can also be used to study the effects of short-range diffusion.

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The DS method has been successfully used to study the properties of hydrogen permeation in a wide spectrum of metals, but difficulties were encountered for aluminium and alloys containing large amounts of this metal. Experiments described by various authors were difficult to reproduce and $D_{\mathrm{eff,H}}$ value obtained for pure aluminium ranged from 3×10^{-6} to 4.5×10^{-10} cm^2/s, depending on the electrolyte composition and saturation parameters [11].

In the case of electrolytic saturation, hydrogen diffusion through metals and alloys also depends on factors such as the potential on the metal–electrolyte interface and the electrolyte pH. The condition of the material surface also has a significant effect. An oxide layer or another coat on the entry surface of a cathodically saturated specimen decreases the hydrogen permeation rate compared to a bare metal, in particular in alkaline solutions [12]. The presence of oxygen in pure alkaline solutions and in solutions containing a chelating agent (an additive t remove iron oxide from the surface and increase the system capacitive reactance) shifts the potential of the entry surface of the iron cathode to more negative values. Conversely, alkaline oxygen-free electrolytes shift this potential to positive values, as found during extended-time cathodic polarisation.

The aim of the present study was to identify suitable electrochemical conditions for accurate measurement of hydrogen diffusivity in iron aluminides using the DS method. Hydrogen diffusivity values were then determined for a range of cathodic currents.

2. Experimental

Tests were carried out on alloys based on an FeAl intermetallic matrix for which the chemical composition is presented in Table 1. We chose an alloy with a stoichiometric composition of Fe–50 at.% Al, a popular alloy containing 40 at.% Al, and an Fe–40 at.% Al alloy with additional alloying elements. The material studied consisted of B2 FeAl iron aluminides obtained by induction melting according to the procedure described by Stępień and Kupka [13]. Ingots of 20 mm in diameter and 70 mm in length were homogenised at 1000 °C for 72 h and slowly cooled in a furnace. Permeability membranes were produced as 2–3-mm-thick slices of the homogenised ingots. The specimens were ground with SiC abrasive paper down to 1200 grit and polished with 3-μm diamond paste. The surfaces were rinsed with distilled water, cleaned ultrasonically in acetone, and dried quickly with air. The hydrogen diffusion process was investigated using a measuring stand equipped with: an ATLAS 9431 potentiostat to automatically maintain an independently varied potential for the sample electrode, a d.c. power supply, a holder to fix the specimen in contact with the solution, and a computer for recording the results.

Fig. 1 shows a block diagram of the set-up for electrolytic saturation and Fig. 2 shows a cross-section of the specimen holder. The measurement system comprised a saturated calomel electrode (Hg/HgCl/KCl) as the reference electrode and an auxiliary electrode in the form of a platinum mesh wound around a cylinder.

The specimen was placed between two connecting Teflon members with conical mounting joints. This facilitated contact between each side of the specimen membrane and each of the electrolytic cells, while maintaining (sealing) each side at the separate electrolytes and cells. The exit side of the membrane was coated with palladium to isolate the FeAl membrane from the NaOH solution and to accelerate ionisation of hydrogen atoms evolving from the membrane. Following a method reported by Zakroczymski [6], membranes were coated with palladium in an aqueous solution containing 0.8 g of $\mathrm{PdCl_2}$ and 60 g of NaOH per dm^3 at a polarisation current density of 200 $\mathrm{A/m^2}$ for 30 s and then 100 $\mathrm{A/m^2}$ for 270 s.

Table 1
Chemical composition of the alloys examined.

Alloy	Content (at.%)				
	Fe	Al	Cr	Zr	B
FeAl	40	60	–	–	–
FeAl	50	50	–	–	–
FeAlCrZrB	54.88	40	5	0.1	0.02

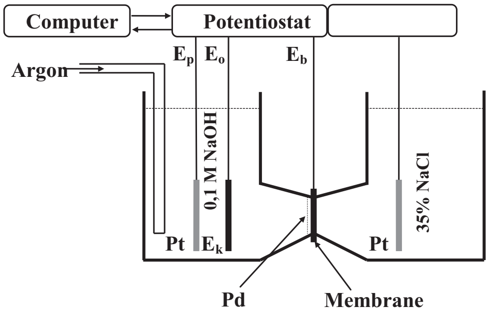

Fig. 1. Experimental scheme for hydrogen diffusivity measurements by the Devanathan–Stachurski method. Eb, electrode investigated (specimen); Eo, reference electrode (calomel, Ek); Ep, auxiliary electrode (platinum mesh); Pd, exit side of the membrane, coated with palladium.

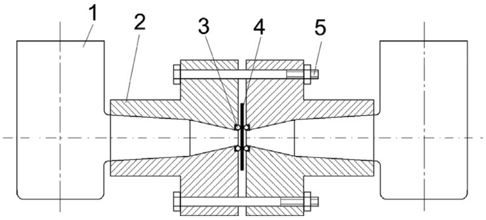

Fig. 2. Electrolytic cells and a cross-section of membrane sample fixture. 1, electrolytic cell; 2, Teflon connecting member; 3, seals; 4, membrane specimen; 5, fixing bolts.

During hydrogenation, the entry side of the membrane was in contact with an appropriate solution and acted as the cathode, while a platinum electrode was the anode. The palladium-coated exit side of the membrane was in permanent contact with 0.1 M NaOH solution, and in this case acted as the anode, while a platinum electrode was the cathode.

The solution on this side of the membrane was deaerated with argon. The saturated calomel electrode was the reference electrode, against which the potentiostat maintained a constant potential of + 50 mV on the membrane exit side. This potential was sufficient to oxidise atoms of adsorbed hydrogen leaving the membrane exit side according to the reaction

$$H_{ads} \rightarrow H^+ + e^- \qquad (1)$$

Under the influence of these electrons, a current of intensity i_p flowed through the platinum electrode, which was recorded with the hydrogenation time t in the form of so-called permeation curve using a computer and a spreadsheet application. The intensity of the anode current i_p is a measure of hydrogen permeation through a membrane of the alloy studied.

Measurements were carried out at room temperature at a constant cathodic polarisation current (saturation current) i_c that was varied in consecutive tests (0.2, 0.4, 0.75, 1.0, 1.5 and 2 A). A thermostat was used to maintain a constant temperature of 293 ± 0.5 K. The active surface area of the membrane was 0.785 cm^2.

The hydrogen concentration in specimens before and after hydrogenation was determined using a Ströhlein Instruments H-mat 2500 hydrogen analyser with sensitivity of 0.01 ppm by weight. The membrane microstructure was observed using a NEOPHOT 2 metallographic microscope and a stereoscopic microscope.