



The influence of vacuum annealing on the uranium–hydrogen reaction



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ABSTRACT

The constant pressure hydriding kinetics of uranium have been measured as a function of temperature for as-polished and vacuum annealed uranium between 65 °C and 385 °C. Enhanced hydrogen reactivity was observed for vacuum annealed uranium between 65 °C and 120 °C and is the result of elevated nucleation kinetics promoting steady state kinetics.

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1. Introduction

The reaction between uranium and hydrogen gives rise to the formation of uranium hydride. The formation of pyrophoric uranium hydride during long term storage has the potential to cause the dispersal of radioactive particles outside suitable containment [1].

The hydriding of uranium has been studied extensively to determine the principle factors responsible for the rate of reaction. The kinetics of the hydriding reaction have been shown to be dependent upon parameters such as the temperature, pressure and nature of the oxide over-layer [2].

The uranium–hydrogen reaction can be considered to consist of four definable periods; the induction, growth, bulk and termination periods. The bulk period exhibits a linear rate of hydrogen consumption once corrected for changes in the reacting surface area that occurs during the course of reaction. Therefore, the bulk period is suited to assessing reaction kinetics. The change in surface area is accounted for by the contracting envelope model proposed by Mintz and Zeiri [3]. Provided a sample reacts evenly on all surfaces the reacting surface area can be related to hydrogen consumption.

It has been previously suggested that the hydriding kinetics of depleted uranium are influenced by the microstructure [4,5]. The rate of reaction is most aggressive with uranium that has received a vacuum annealing pre-treatment, which was attributed thermally induced changes in the microstructure. The correlation between microstructure and rate has recently been questioned and it has been suggested that the elevated reactivity is the result of enhanced nucleation kinetics [6]. In the present study the reaction kinetics of wrought depleted uranium under a constant 1 bar

hydrogen pressure has been evaluated as a function of temperature for as-polished and vacuum annealed uranium.

2. Experimental

This work used wrought depleted uranium coupons (12 × 12 × 0.75 mm) with the following impurities: C (50 ppm), Fe (22 ppm), Al (5 ppm), Ni (15 ppm), Cr (1 ppm) and Si (2 ppm).

Samples were electro-polished using a current density of 0.28 A cm⁻² for 40 s in an equivolume solution of distilled water and concentrated sulphuric and phosphoric acids then rinsed with deionised water and iso-propyl alcohol. Samples were then placed in a stainless steel reaction vessel immediately after electro-polishing and evacuated at room temperature using a gas handling line with a base pressure of 1 × 10⁻⁶ mbar. Using a tube furnace to heat the reaction vessel, annealed samples were heated to 640 °C under a dynamic vacuum for 8 h then cooled to the reaction temperature before exposure to ultra pure hydrogen (stored over LaNi₅) at constant pressure. As-polished samples were heated to the reaction temperature before exposure to hydrogen. Type K thermocouples and MKS BaratronTM were used to monitor temperatures and pressures. The consumption of hydrogen was recorded using an MKS flow meter. Readings were recorded periodically throughout the experiments using a Data Scan unit and OrchestratorTM software.

Sample microstructures, analysed before and after vacuum annealing indicated an 8 h anneal was of insufficient time to afford grain growth although an 8 h treatment would be sufficient to remove some of the twinning defects present. Significant grain growth was only observed with samples vacuum annealed for >48 h.

3. Results and discussion

Estimates of rates of reaction can be obtained for the hydriding reaction of uranium from the rate of hydrogen consumption. The variation in reaction fraction (α) as a function of time obtained from constant pressure hydriding experiments on annealed and as-polished uranium are shown in Fig. 1.

Provided steady state conditions exist, i.e. a coherent reaction front exists across the entire surface, the data sets shown in Fig. 1 will provide satisfactory estimates of the hydriding rate (V). For the regular geometrically shaped samples used in this

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study values of V can be determined using Eq. (1). The rate of hydrogen consumption was measured using a flow meter and is reported in $\text{cm}^3 \text{min}^{-1}$ (Fig. 2). Assuming a coherent reaction front for the samples size used in this study, a consumption rate of $1 \text{ cm}^3 \text{min}^{-1}$ of hydrogen is equivalent to a hydriding rate of ca $0.025 \mu\text{m s}^{-1}$ or $3 \text{ mmol m}^{-2} \text{s}^{-1}$, this is in agreement with the application of Eq. (1) to the data in Fig. 1.

$$V = \frac{dz}{dt} \frac{L}{2} \quad (1)$$

where, V is the hydriding rate ($\mu\text{m s}^{-1}$), α is the reaction fraction, t is time (s) and L is sample thickness (μm).

The uranium–hydrogen reaction occurs sequentially through four periods of reaction, the induction, acceleration, bulk and termination periods. Importantly the bulk period occurs once a coherent reaction front has been formed across the entire surface of the sample and is characterised by steady state (linear) kinetics. It is informative to assess the rate of hydrogen consumption for annealed and as-polished uranium against the four periods of reaction (Fig. 2). The as-polished samples did not experience steady state kinetics and by inference a bulk period of reaction. Instead, the acceleration period proceeded directly to the termination period. The acceleration period involves the nucleation and growth of

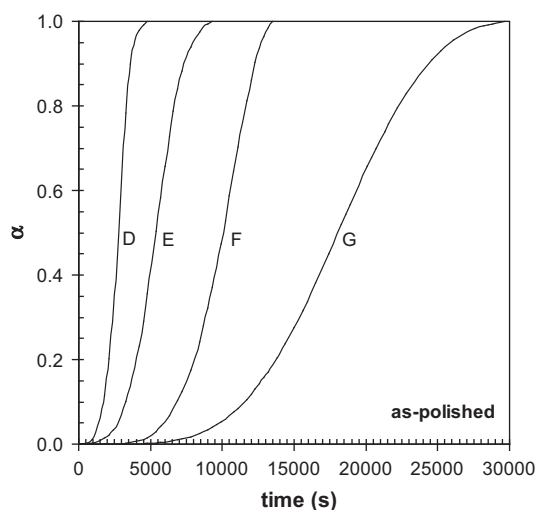
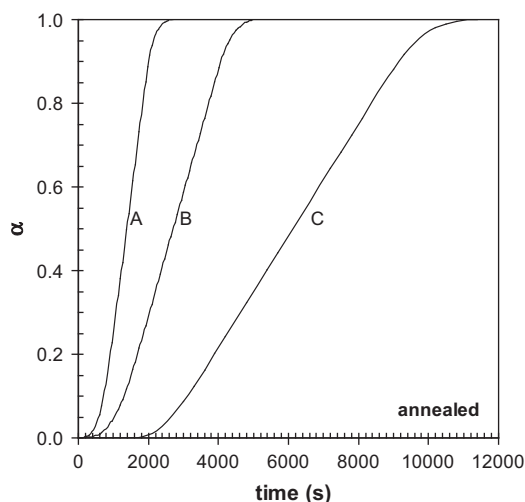


Fig. 1. Variations in the reaction fraction (α) as a function of time under a constant hydrogen pressure of 1 bar. Samples A, B and C are annealed samples reacted at 110, 85 and 68 °C. Samples D, E, F and G are as-polished samples reacted at 120, 100, 85 and 66 °C.

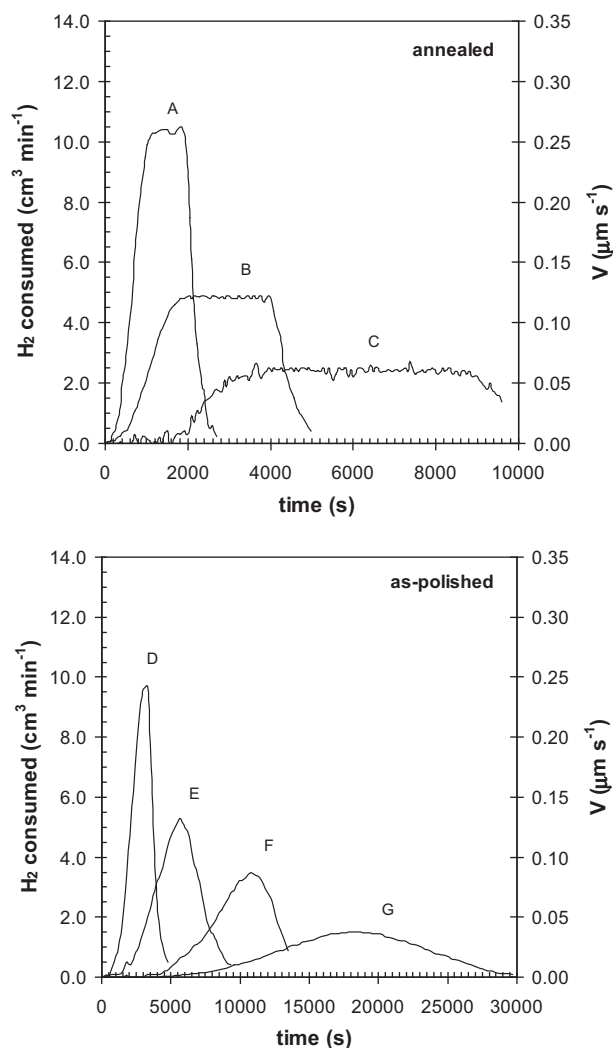


Fig. 2. Variations in the hydrogen consumption as a function of time under a constant hydrogen pressure of 1 bar. Samples A, B and C are annealed samples reacted at 110, 85 and 68 °C. Samples D, E, F and G are as-polished samples reacted at 120, 100, 85 and 66 °C. The secondary y axis indicates the hydriding rate (V) in units of $\mu\text{m s}^{-1}$. Note: since Eq. (1) is not valid for the as-polished samples, values in $\mu\text{m s}^{-1}$ should only be used for qualitative comparisons with other work.

discrete hydride reaction sites. A direct transition from the acceleration period to the termination period would suggest both nucleation and growth mechanisms occurred throughout. The vacuum annealed samples exhibit steady state reaction conditions i.e. a bulk period of reaction, which suggests the samples reacted evenly on all surfaces. Under this assumption, the reacting surface area can be approximated from the starting geometry and Eq. (1) is valid. Steady state conditions were not observed with as-polished uranium suggesting a coherent surface coverage was not achieved. Consequently, the actual reacting surface area cannot be related to the starting geometry of the samples and Eq. (1) is not valid. Therefore, although a difference in rate maxima under equivalent reaction conditions is observed between as-polished and annealed uranium, this difference reflects the total area of the reaction interface. As a consequence of slow nucleation kinetics with as-polished uranium, the reaction interface is smaller and hence the rate appears slower.

The temperature dependence of the maximum hydriding rates (V_{max}) observed during reaction under a constant 1 bar hydrogen pressure for as-polished and annealed samples is given in Fig. 3. A clear difference in the rate maxima below 150 °C

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