Journal of Nuclear Materials 449 (2014) 49–53

Contents lists available at ScienceDirect

Journal of Nuclear Materials

journal homepage: www.elsevier.com/locate/jnucmat

Effect of niobium additions on initial hydriding kinetics of uranium

Ruiwen Li *, Xiaolin Wang

China Academy of Engineering Physics, P.O. Box 919-71, Mianyang 621900, Sichuan, China

ARTICLE INFO

Article history:
Received 18 August 2013
Accepted 28 February 2014
Available online 11 March 2014

ABSTRACT

To study the behavior of hydrogen corrosion at the surface of U, U–2.5 wt%Nb alloy and U–5.7 wt%Nb, a gas–solid reaction system with an in situ microscope was designed. The nucleation and growth of the hydride of the alloy were continuously observed and recorded by a computer. The different characteristics of the hydrides on U metal and U–2.5 wt%Nb showed that the later alloy is more susceptible to hydrogen corrosion than the former. The growth rate of hydride of U–2.5 wt%Nb, calculated by measuring the perimeter of the hydride spots recorded by the in situ microscope, exhibited a reaction temperature dependency in the range of 40–160 °C, for pressure of 0.8×10^5 Pa. An Arrhenius plot for growth rate versus temperature yielded activation energy of 24.34 kJ/mol for the hydriding of U–2.5 wt%Nb alloy. The maximum hydriding rate was obtained at 125 °C, whose thermodynamics reason was discussed.

1. Introduction

Uranium and its alloys have been widely used in the field of nuclear engineering: nuclear power, armor-piercing ammunition, and nuclear weapon. However, due to its reactivity to environment atmosphere, especially hydrogen, the surface corrosion on U have been seriously concerned from the beginning of its use. Hydrogen attack to uranium usually results in such problems as hydride burning, strength weakening, and hydrogen corrosion. Sometimes, the amount of hydrogen gas is not so much because it mainly comes from decomposition of macromolecule materials or water in air. So, the initiation of hydrogen corrosion of U in the environment containing a small quantity of H_2 has been generally studied. Gouder, Fu and Wang give the valence band and core level spectroscopy of UH_3 [1,2]. Valence band spectra showed that UH_3 is metallic, and 5f electrons are itinerant. U 4f core level spectra of UH_3 showed a main peak at slightly higher binding energy than U metal. The works by Gouder and Ao confirmed the formation of β-UH_3 at low temperature after U hydriding [1,3]. Ab initio calculations were made to investigate thermodynamics, hydrogen saturation and phase transformation of uranium–hydrogen system [4–7]. The result showed that volume-expanded due to the formation of UH_3 phase is the primary kinetic barrier to hydride formation. Many works have been focused on the initial kinetics of hydriding of U [8–16], for example, Mintz and Glascott developed a uranium hydride formation models in which the oxide overlayer acts a barrier to hydrogen diffusion. However, the reaction kinetics of U–H_2 has been shown to vary widely from study to study due to its dependence on a variety of factors. These factors that are apparently difficult to replicate or control include the surface characteristics of the uranium metal and the presence of gaseous impurity. Previous references showed that adding niobium to uranium can improve the anti-oxidation of U, and strengthen the mechanics properties. Yet, there is little information concerning the hydrogen corrosion of U–Nb alloy. In this work, the influence of alloying of uranium on the initial kinetics of hydriding was focused.

2. Experimental and materials

A reaction cell with a quartz window was designed. Facing the vertically window, an in situ microscope model HIROXKH-7700 was positioned, which can record the morphology change of hydride formation on sample. The experimental device is given in Fig. 1. A tube furnace surrounded the reaction cell so that the sample was heated to equivalent temperatures. Thermocouple was mounted in the center of the reaction vessel to monitor the temperature of specimens. Temperature was monitored and maintained constant to within ±1 °C using a temperature programmed controller. The pressure was continuously measured with a computer-based data acquisition system to determine the subtle change. High pure hydrogen (99.999%) was used for the reaction studies, which was obtained from a LaNi5H*x* bed. U, U–2.5 wt%Nb and U–5.7 wt%Nb alloy used here were made by casting, annealing, and then cut to pieces with Ø10 × 3 mm. The final structure of U–2.5 wt%Nb alloy is a double phase composition of $(\alpha + \gamma_{1-2})$ with pearlite banded structure. By the annealing process of U–2.5 wt%Nb in this work, the percentage of α and γ_{1-2} phase

* Corresponding author. Tel.: +86 816 3626742; fax: +86 816 3625900.
E-mail address: ruiwenli@163.com (R. Li).

http://dx.doi.org/10.1016/j.jnucmat.2014.02.036
0022-3115/

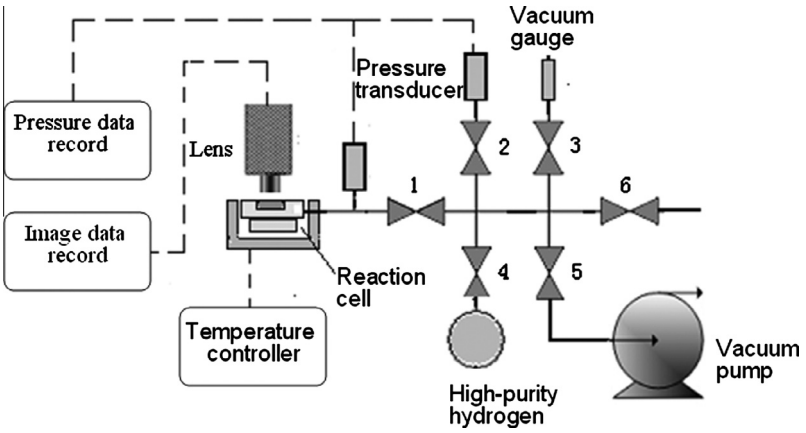

Fig. 1. The schematic figure of the experimental device.

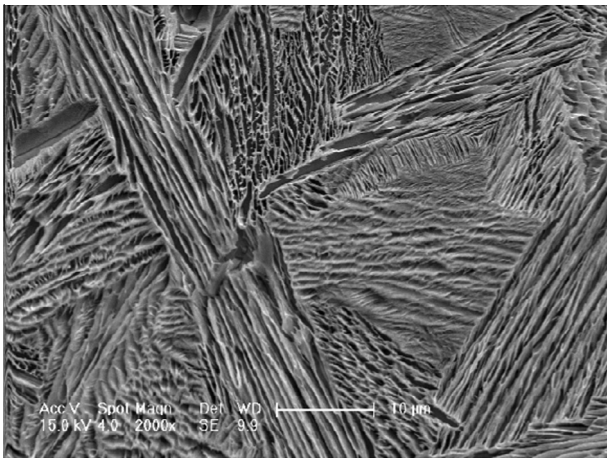

Fig. 2. Double phase microstructure of U–2.5 wt%Nb alloy after being etched.

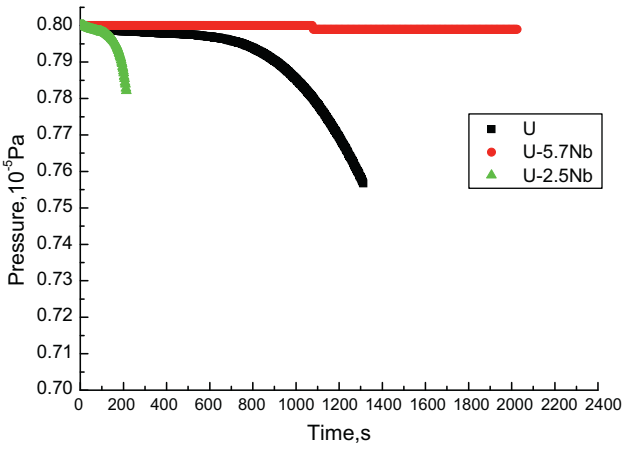

Fig. 4. Pressure change of U, U–2.5 wt%Nb and U–5.7 wt%Nb reaction with H_2 at same temperature (125 °C).

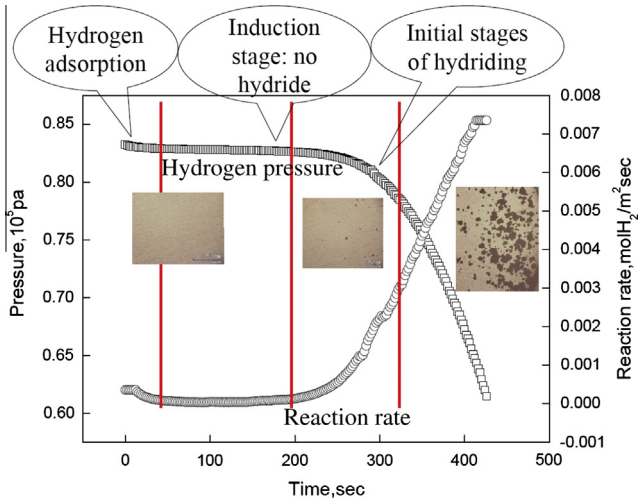

Fig. 3. The initial kinetics of U–2.5 wt%Nb reaction with H_2: hydrogen pressure, reaction rate, and morphology change with time, $T = 80$ °C, $P = 0.83 \times 10^5$ Pa.

are 50%, 50% respectively, seen in Fig. 2. The Nb content in α phase is about 1%, which is less than that in γ_{1-2} phase(19.5%). U–5.7 wt%Nb is an α″ martensite and α-U is a orthorhombic crystal system. Before the sample was loaded in the cell, it was mechanically polished to a mirror-like surface. The reaction cell was then evacuated to a vacuum of 10^{-3} Pa for 1 h. The sample was then heated up to a temperature of 170 °C under vacuum to outgas for 1.5 h, which was named preheating in many references. Then, the samples were corroded more quickly by high pure hydrogen at different temperatures, for pressure of 0.8×10^5 Pa. For a better comparison of U–2.5 wt%Nb with U and U−5.7 wt%Nb, the pretreatment processes of hydriding of them were ensured in the same.

3. Results and discussion

3.1. The initiation of hydride formation

To comprehensively reveal the initial kinetics of hydriding, such kinetics parameters as hydrogen pressure, hydrogen consumption rate, induction period, and hydride sites were determined integrally, seen in Fig. 3. Unlike hydriding of other metals, there is an induction period before hydride formation on U materials. After the induction period (during which there is no measurable pressure change and no hydride site), about a few minutes, some hydride nuclei occur on the surface. Hydrogen corrosion reactions occur at the limited region near the surface, which was proved by the cross sections detection by SEM and OM .At the same time, hydrogen pressure (left coordinate in Fig. 3) begin to drop slowly, and reaction rate (right coordinate in Fig. 3) increase non-linearly, as shown in Fig. 3. With the consumption of hydrogen, more and