



Effect of aluminum on hydrogen absorption kinetics of tantalum



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ABSTRACT

The isothermal hydrogen absorption kinetics of Ta_{1-z}Al_z alloys ($z = 0, 1, 1.6$ and 2.4 atom%) has been investigated in the temperature range of 673–973 K. The reacted fractions of hydrogen as well as reaction rate constant have been determined from time dependent hydrogen absorption curves using pressure drop method. The variation in rate constant with respect to temperature has been observed for all the alloys. Three-dimensional diffusion processes seems to be the intrinsic rate limiting step of hydrogen absorption. The apparent activation energy of hydrogen absorption has been calculated using Arrhenius equation. With increasing aluminum concentration, the hydrogen absorption kinetics slows down. Consequently, the rate constant decreases and the apparent activation energy of hydrogen absorption increases. The apparent activation energy of hydrogen absorption increases from 53.7 to 57.7 kJ/mol with increasing Al concentration from 0 to 2.4 atom% in tantalum.

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1. Introduction

Hydrogen is a clean, non-polluting and renewable energy carrier alternative [1–5]. From application points of view, the production, separation, storage and recovery of hydrogen are the cornerstones to “Hydrogen Economy” [6–10]. The pure hydrogen gas is produced mainly by passing gas mixture through a hydrogen permeation membrane [11]. This has generated a continuing interest in developing the economically feasible methods for the hydrogen separation. The ideal hydrogen separation membrane should have high hydrogen permeability and good mechanical properties. Various researchers have tried to develop low cost and high performance non-Pd based alloys for hydrogen separation membranes [11–19].

Tantalum has large hydrogen solubility and diffusivity and considered to be a potential candidate material for the hydrogen separation membrane operating in a flowing gas system in a wide range of temperature and pressure for the purification of hydrogen from a gaseous mixture [9,11,12,20–22]. Compared to Pd, the commonly used hydrogen separation membrane material, Ta is cheaper and possesses order of magnitude higher hydrogen permeability [21,23–28]. High hydrogen solubility of tantalum leads to expansion of the metal lattice, creating stresses which cause the metal to become brittle. Hydrogen embrittlement is the main limitation of tantalum metal to be commercially recognized it as a hydrogen separation membrane [25,28–32]. Therefore, reducing

the hydrogen solubility by adding alloying elements could be thought as a way to retain the mechanical strength of the membrane during its usage [12,33]. The effect of aluminum has been reported on solubility as well as on hydrogen absorption kinetics in group IV and V metals/alloys [14,17,18,33–38]. In all these alloys, the observed solubility and permeability is lesser than in their corresponding pure unalloyed state. The resistance to hydrogen embrittlement and strength of these alloys are much better than corresponding pure metal while permeability is still greater than the leading palladium alloy [28]. As per author’s knowledge, the effect of aluminum on the hydrogen absorption kinetics in tantalum has not previously been reported in the literature. Thus, it is important to understand the behavior of aluminum as an alloying element on the hydrogen absorption kinetics in tantalum metal. In the present study, the influence of aluminum on the kinetics of hydrogen absorption in tantalum is investigated in the temperature range of 673–973 K.

2. Experimental methods

2.1. Sample preparation

The Ta_{1-z}Al_z alloys ($z = 0, 1, 1.6$ and 2.4 atom%) were prepared using highly pure (>99.8%) tantalum and aluminum foils (Aldrich) by arc melting technique. The aluminum concentration was chosen so as to keep the alloys within their solid solubility limits and avoid fragmentation due to hydrogen induced embrittlement [39,40]. Pure Ta, Ta–1Al, Ta–1.6Al and Ta–2.4Al are used as abbreviation everywhere in the text for 0, 1, 1.6 and 2.4 atom% Al in Ta, respectively. The alloys obtained in button form were cold rolled to 0.4 mm thickness and cleaned with acetone. The chemical analyses of the alloys were carried out using Glow Discharge-Quadrupole mass Spectrometry (GD-QMS). The detailed chemical compositions of all the alloys are

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mentioned in Table 1. Phase characterization of these alloys was performed by X-ray diffraction (XRD) technique using Cu K α radiations of Bruker D8 diffractometer. The specimens for hydrogen charging were cut into $0.4 \times 10 \times 15$ mm³ dimension using EDM cutting machine. Before hydrogen incorporation, all the samples were cleaned chemically using an acidic solution (HF:HNO₃:H₂SO₄ :: 2:2:5) and polished mechanically on emery papers followed by cleaning with acetone. Hydrogen charging was carried out in a Sievert's apparatus. The hydrogen generator (model: CIC-PW-SPE500HC) was used as a source for 5 N (99.9995%) pure hydrogen gas from which required amount of hydrogen could be released.

2.2. Kinetic measurements

A constant volume and variable pressure method was used to study the hydrogen absorption kinetics of Ta_{1-z}Al_z alloys. The Sievert's apparatus used for hydrogen charging has been discussed in details in our previous papers [40,41]. Kinetic parameters of hydrogen absorption in these alloys were determined by conducting experiments under isothermal heating condition in a temperature range of 673–973 K. The sample was kept in the reaction chamber which was put inside a moveable furnace. A high vacuum of the order of 10⁻⁶ torr was created inside the system using rotary and diffusion pumps. The sample surface was activated before hydrogen absorption [40] and heated to the preset temperature at a rate of 10 K/min. After the required temperature was achieved and stabilized, high pure (5 N) hydrogen gas was introduced inside the reaction chamber at a pressure of 760 torr. The drop in system pressure with respect to time is a measure of the degree of absorption of hydrogen in the alloys. After a time lag, the system pressure became constant. When constant pressure was observed continuously for more than 24 h at any fixed temperature, it was assumed that equilibrium has been achieved in the system with respect to the hydrogen content of the matrix.

2.3. Kinetic equation

The kinetics of hydrogen absorption in a metal is affected by temperature, pressure, surface properties of the materials and the presence of other elements like substitutional impurities [36]. The reaction mechanism for absorption of hydrogen in metals and alloys involves several steps which are listed as follows [42–45]: gas-phase mass transport of hydrogen on the alloy surface, physisorption of hydrogen gas molecules, dissociation of hydrogen molecules into atomic form and chemisorptions on the surface, surface penetration and diffusion of hydrogen atoms; and hydride formation. A schematic representation of hydrogen absorption mechanism is shown in Fig. 1.

The slowest step among these steps is the rate determining step. Generally the method used to study the kinetics is to fit the time dependent reacted fraction (α) to various analytical rate expressions, through which reaction mechanism and intrinsic rate limiting steps are determined. The rate equation for the kinetics of solid–gas reaction is expressed as follows [36,46]:

$$\frac{d\alpha}{dt} = kf(\alpha) \quad (1)$$

where, α is the reacted fraction at time t , k is rate constant, $f(\alpha)$ is a function determining the mechanism of the reaction and $g(\alpha)$ is the integral form of $f(\alpha)$, given by

$$g(\alpha) = \int \frac{d\alpha}{f(\alpha)} = kt \quad (2)$$

$f(\alpha)$ and $g(\alpha)$ refers to the reaction mechanism functions including nucleation and nuclei growth, phase-boundary controlled reactions, chemical reactions and diffusion. There are 42 reaction mechanisms given in the literature [47]. Based on the experimental data of hydrogen absorption curve, the reacted fraction, α can be calculated as follows:

$$\alpha = \frac{p_0 - p_t}{p_0 - p_{eq}} \quad (3)$$

where, p_0 is the initial pressure, p_t is the pressure at time t and p_{eq} is the final equilibrium pressure.

The function $f(\alpha)$ or $g(\alpha)$ giving the best linearity with time is considered as the mechanism for hydrogen absorption in Ta_{1-z}Al_z alloys. The rate functions of hydrogen absorption and the kinetic parameters, k , are obtained from the linear regression fitting. The apparent activation energies for hydrogen absorption in these alloys are calculated using Arrhenius equation.

Table 1
Chemical composition of Ta_{1-z}Al_z alloys (atom%).

Alloys	Al	O	N	C
Pure Ta	0	0.10	0.06	0.03
Ta–1Al	1.0	0.15	0.06	0.02
Ta–1.6Al	1.6	0.18	0.03	0.03
Ta–2.4Al	2.4	0.17	0.01	0.04

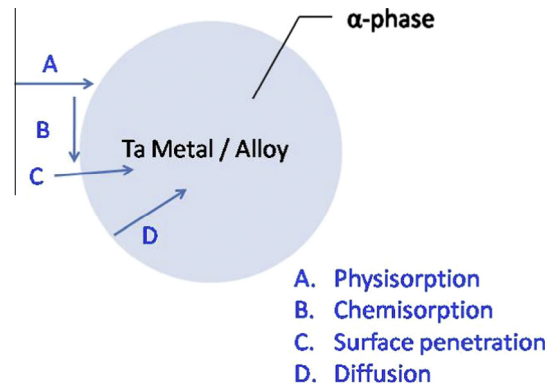


Fig. 1. Schematic representation of hydrogen absorption mechanism.

3. Results and discussion

3.1. General observation

The XRD pattern of unalloyed Ta foil shows bcc structure and matches quite well with PCPDF # 01-1309. All tantalum–aluminum alloys are solid solution of Ta i.e. single phase bcc structures as revealed in their XRD patterns in Fig. 2. It has been observed that with increasing Al content in Ta, XRD peaks shift towards the higher 2θ values. The inset in Fig. 2 clearly shows the shifting of (200) peak with increasing Al content. This indicates that the lattice parameter of Ta_{1-z}Al_z matrix decreases with increasing Al content. The lattice constant for Ta–Al alloys are shown in Table 2.

3.2. Hydrogen absorption curve

The isothermal hydrogen absorption curves for Ta_{1-z}Al_z alloys at different temperatures are shown in Fig. 3. In the studied temperature range (673–973 K), equilibrium pressure has been attained within 6 h of processing (hydrogen charging) time. The time required for achieving equilibrium decreases with temperature whereas the equilibrium hydrogen pressure increases with increasing temperature as shown in Fig. 3. Moreover, hydrogen pressure drop decreases with temperature as well as with increase in Al content that result in decrease in hydrogen solubility in these alloys. The data in Fig. 3 indicate that the hydrogen absorption kinetics in Ta_{1-z}Al_z alloys becomes faster with temperature but slower with increase in Al content.

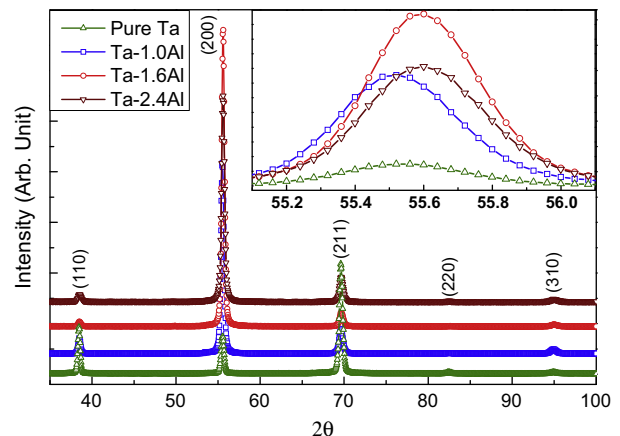


Fig. 2. XRD pattern of Ta_{1-z}Al_z alloys ($z = 0, 1, 1.6$ and 2.4 atom%). The inset shows the shifting of (200) peak with increasing Al content.

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