ABSTRACT

Tantalum is a potential candidate material for the hydrogen separation membrane due to its large hydrogen solubility and good hydrogen diffusivity. The permeability is a product of solubility and diffusivity. The hydrogen solubility in tantalum and its alloys is one of the parameters responsible to estimate the permeability. The hydrogen embrittlement associated with tantalum at low temperature is the main limitation of its use in membrane applications. Alloying with the elements which are having less hydrogen solubility or destabilize the hydrides can be a way to overcome this limitation. In the present work, the effect of nickel, chromium, iron and aluminium on the solubility of hydrogen in tantalum has been investigated. Ta-alloys with Ni, Cr, Fe and Al within solid solubility limit were prepared using arc melting in an inert atmosphere. Pressure-composition-isotherms (P-C-T) equilibrium measurements have been investigated in the temperature range (673-873) K for Ta-H and Ta-M-H systems [M = Ni, Cr, Fe and Al] using a Sievert’s apparatus. The dissolved hydrogen was within the solid solubility range corresponding to the temperature and followed the Sievert’s law. From the equilibrium P-C-T data, the thermodynamic parameters: the relative partial molar enthalpy, entropy and Gibb’s free energy for the solution of hydrogen in these alloys are evaluated using Sievert’s relationship. The hydrogen solubility in tantalum-alloys decreases with increase in the alloying elements composition. This decrease in solubility is attributed to increase in lattice strain energy of the alloys or due to very less solubility of hydrogen in these elements or the chemical inertness of these alloying elements towards the hydrogen. The relative partial molar enthalpy becomes less negative with increase in alloying elements composition whereas entropy values are almost constant.
In addition, the isothermal hydrogen absorption kinetics of unalloyed tantalum and tantalum-aluminium alloys has been investigated in the temperature range of (673-973) K. The reacted fraction of hydrogen, $\alpha$, was calculated from the experimental data of hydrogen absorption in different tantalum-aluminium alloys as a function of time using pressure drop method. The function $g(\alpha)$, giving the best linearity with time is indicative of the mechanism of hydrogen absorption. The rate function of hydrogen absorption and the kinetic parameters are obtained from the linear regression fitting of $g(\alpha)$ versus time plots. The mechanism of three-dimensional diffusion is the intrinsic rate-limiting step of hydrogen absorption processes in the studied temperature range. The apparent activation energy for the absorption of hydrogen in these alloys also calculated using Arrhenius equation that increases linearly with increase in the aluminium content in the alloys.

The thermodynamic and kinetics data for the solution of hydrogen in tantalum and its alloys can be used to process the design for Ta-based materials for various hydrogen atmosphere applications and can also be utilized in various modeling studies for hydrogen solubility and permeability.

**Keywords:** Tantalum; Alloying elements (Ni, Cr, Fe and Al); Hydrogen solubility, Sievert’s constant, Thermodynamics parameters, Hydrogen absorption kinetics, Activation energy.
SYNOPSIS

Introduction

The development of hydrogen based energy utilization is attractive in view of attendant benefits such as reduction in the global warming and minimization of investment in infrastructure and energy cost [1]. In this situation, the advances in the technology for production, purification, storage and supply of hydrogen will become increasingly important [2-3]. Hydrogen separation techniques also find applications in chemical, petrochemical, microelectronic industries, fuel cells and “Vision 21” program of DOE [4-5]. This is creating a persistent interest in developing economically feasible methods for the hydrogen purification/separation. However, the development of hydrogen separation membrane is an important technical issue. The rapid development of membrane reactors and fuel cells has witnessed increasing interest in dense composite membranes for hydrogen separation and purification [6-7]. The ideal hydrogen separation/purification membrane should have high hydrogen permeability and good mechanical properties [8] and should be capable of functioning in a flowing gas at high temperature and high pressure. Tantalum is a promising material as a component in hydrogen separation membranes operating at a range of temperatures and pressures [4, 7, 9]. It has high hydrogen permeability [4]. Compared to palladium, it is cheaper and possesses order of magnitude larger hydrogen permeability [4].

Literature Review

Two main limitations of tantalum metal to be commercially usable as a permeable membranes material are its tendency for surface oxidation and for hydrogen embrittlement [4, 7-8]. Surface oxidation of tantalum can be minimized by coating with
Pd [10]. Hydrogen embrittlement problem arises from the change of lattice parameter or formation of hydrides [10]. Therefore, for a given temperature and pressure, reducing the hydrogen solubility could be considered as an approach to preserve mechanical properties of the membrane [11]. Alloying can be an effective way to control the hydrogen solubility without varying other parameters like temperature or hydrogen pressure. The effect of Fe, Al, Ni, Cr, Mo, Cu, Pd, and Sn on the solubility and permeability of group V elements, vanadium and niobium have been earlier investigated and reported in the literature. In all of these cases, the experiential solubility and permeability is inferior to that of pure metal. Importantly, however, the embrittlement resistance and durability of these alloys are much better than the pure metal, while the permeability is still greater than the leading palladium alloy [11-16]. As permeability is a product of solubility and diffusivity, therefore, measuring the solubility of hydrogen in Ta and its alloys highlights one of the parameters that determines the permeability. Moreover, the solubility measurement also helps to obtain thermodynamic parameters for the solid solution of hydrogen in tantalum and its alloys.

Thermodynamic quantities for Ta-H system have been reported by many investigators using experimentally determined P-C-T curves and it was found that the relative partial molar enthalpies, $\Delta H_H$, and entropies, $\Delta S_H$, of hydrogen are virtually constant with respect to temperature for a given concentration in the considered temperature range [17-24].

The present work aims to evaluate the effect of Ni, Cr, Fe and Al (within solid solubility limit in Ta matrix) as alloying element on the solubility of hydrogen in bcc tantalum and on the thermodynamic parameters of Ta-H system. This information has not been previously reported in the literature. Solid solution alloys avoid the hydrogen
embrittlement which occurs in a two-phase alloy. Isothermal as well as isobaric P-C-T equilibrium measurements have been investigated in the temperature range of 673 – 873 K and the hydrogen pressure range of 0.6-1.2 atmospheres for tantalum and its solid solution alloys mentioned above at different compositions. The thermodynamic parameters - relative partial molar enthalpy, entropy and Gibb’s free energy for solutions of hydrogen in tantalum alloys were also calculated.

**Experimental Techniques**

**Sample Preparation**

Various alloys of tantalum (Ta-Al, Ta-Cr, Ta-Fe and Ta-Ni) within solid solubility range were prepared using arc melting in an inert atmosphere. To prepare these alloys, high purity (>99.8%), Aldrich make tantalum foil and Al, Cr, Ni and Fe thin sheets were used. The melting was repeated 6-10 times to make the alloys homogeneous. The alloy was obtained in a button form. It was cold rolled to 0.3 mm thickness and cleaned with acetone. After rolling, the sheets were cut into small specimens using an EDM cutting machine. Before hydrogen charging, all the samples were cleaned chemically using an acid solution (HF:HNO₃:H₂SO₄::2:2:5) and mechanically polished on emery paper followed by cleaning with acetone. The homogeneity of the alloys was checked by measuring their Vickers Hardness and by line scans SEM-EDS analysis. The elemental compositions of all samples were analyzed by Glow Discharge - Quadrupole mass Spectrometry (GD-QMS). Phase characterizations of the alloys were performed using X-ray diffraction (XRD).
**Hydrogen Charging**

A Sievert’s apparatus was used for both hydrogen solubility and kinetic studies. The sample was placed into a quartz sample holder which was then kept inside the reaction chamber. A high vacuum, of the order of $10^{-6}$ torr, was created inside the system using rotary and diffusion pumps. The sample was heated at 1183 K under this high dynamic vacuum condition to activate the sample surface. The system was backfilled with hydrogen and then cooled down to room temperature. The temperature was further raised to 1183 K and then system was re-evacuated to $10^{-6}$ torr to release the entire hydrogen from the sample. This process was repeated several times. The process is commonly employed to activate the sample before hydrogen charging by introducing micro cracks. The sample was then cooled up to the required temperature. To obtain isothermal PCT curves, hydrogen was introduced into the system from the hydrogen generator at the constant temperature and to a predetermined pressure level (initial pressure reading). The sample started absorption of hydrogen at a fixed temperature and drop in the system pressure was observed. After some time, pressure inside the system became constant. When constant pressure was observed continuously for 24 hrs, then it was assumed that equilibrium has been achieved in the system (final pressure reading). Equilibrium values were confirmed by repeating the cycles. At the end of the run, the furnace was switched off and removed away from the reaction chamber and the valve connecting the sample holder to the remaining system was disconnected. The reaction chamber was rapidly cooled by quenching so that hydrogen absorption during cooling could be minimized. Sample was taken out from the tube. The amounts of hydrogen dissolved in the samples were determined by inert gas fusion technique, and the results were checked against the value obtained by pressure drop method.
To investigate the kinetics of hydrogen absorption in the Ta-Al alloys, the changes in pressure values with time at a constant temperature were noted and the fraction reacted / fraction absorbed ($\alpha$) of hydrogen was calculated.

**Results and Discussion**

*Effect of Ni, Cr, Fe and Al as alloying elements on the solubility behavior of hydrogen in tantalum*

XRD pattern of Ta-alloys indicated that all the alloys are single phase bcc solid solution. Addition of the alloying elements to tantalum shifted the pure Ta peaks toward the higher 2θ values which indicate that lattice parameter of Ta has decreased on the addition of these elements. Scanning Electron Microscopy (SEM) and EDS analysis of alloys indicate that alloys are homogeneous and there is no other phase formation. Ta-H phase diagram [17], shows that at temperature higher than 334 K, a single homogeneous $\alpha$-phase exists in which metal atoms occupy a bcc lattice. In our study, all the experiments are carried out at temperature above 334 K and the dissolved hydrogen is observed within the solid solubility limit and following the Sievert’s law which states that

$$c \propto p^{1/2}$$

or

$$c = K_s \sqrt{p}$$

or

$$K_s = c / \sqrt{p}$$
Where, \( c \) is the amount of dissolved hydrogen, \( p \) is the hydrogen gas pressure, and \( K_s \) is the Sievert’s constant.

The square root dependence follows from the fact that hydrogen dissolves in atomic form in the host matrix [12]. The effects of alloying elements are observed in isobaric as well as in isothermal P-C-T measurements which indicate that solubility of hydrogen in Ta decrease with increasing content of alloying elements. That the dissolution follows Sievert’s law is confirmed from the linear behavior of isothermal P-C-T curves.

The decrease in hydrogen solubility may be due to change in strain energy of dissolved hydrogen due to presence of different size interstitial sites around a substitutional atom. It may be attributed to repulsive interaction between H and alloying atoms [15]. According to Pauling, the atomic radii of Ta, Ni, Cr, Fe and Al are 146, 124, 128, 126 and 143 pm respectively. The lattice parameter of Ta decreases with the addition of these atoms. Therefore, the lattice size and interstitial sites size decrease and hence solubility decrease. The decrease of hydrogen solubility in Ta-alloys could be explained due to increase in lattice strain energy as proposed by Brodowsky [25]. The change in electronic structure may also be responsible for change in the hydrogen solubility. The electronic effects appear to be more important in controlling the overall solubility in the matrix. Several investigators have discussed the possibility of a correlation between the effective free electron concentration of an alloying addition and its effect on the solubility of hydrogen in base metal. Hence, for given hydrogen pressure, if partial molar enthalpy of electrons is increased on the addition of alloying elements, the concentration of dissolved hydrogen will decrease. In the present study, electron factor does not seem to be
more important, the electronegativity of Ta being smaller than all of these alloying elements (Ni, Cr, Fe and Al).

**Thermodynamic parameters for the solubility of hydrogen in Ta and Ta-alloys**

The $K_s$ values were calculated using Sievert’s law for the solution of hydrogen in Ta and Ta-alloys at three different temperatures and at one atmosphere hydrogen pressure. The Sievert’s constant ($K_s$) is related with change in enthalpy, $\Delta H_H$ and change in entropy, $\Delta S_H$ of the solution for hydrogen [26] by the following relations,

$$K_s = \frac{c}{\sqrt{p}} = \exp\left(\frac{-\Delta H_H}{RT}\right) \exp\left(\frac{\Delta S_H}{R}\right)$$

or

$$\log K_s = \log\left(\frac{c}{\sqrt{p}}\right) = -\frac{\Delta H_H}{4.575T} + \frac{\Delta S_H}{4.575}$$

From the slope and intercepts of $\log K_s$ vs $1/T$ (K) plots, the values of relative partial molar enthalpy and entropy of solution of hydrogen can be calculated. The relative partial molar Gibb’s free energy is related with the relative partial molar enthalpy, $\Delta H_H$ and the relative partial molar entropy, $\Delta S_H$ by the following relation:

$$\Delta G_H = \Delta H_H - T\Delta S_H$$

Thus, using the $\Delta H_H$ and $\Delta S_H$ values, the relative partial molar Gibb’s free energy could also be calculated at different temperatures. The enthalpy of solution for hydrogen in tantalum is increasing with increase in the content of alloying element in tantalum matrix while entropy values are nearly constant.
Hydrogen absorption kinetics of Ta-Al alloys

The reaction mechanism for the absorption of hydrogen in the metals and alloys involves the following steps: gas-phase mass transport of hydrogen on the alloy surface, physisorption of hydrogen gas molecules, dissociation of hydrogen molecules into atomic form and chemisorption on the surface, surface penetration of hydrogen atoms, hydrogen atoms diffusion through the hydride layers and hydride formation.

The slowest among these steps is the rate determining step. Generally the method used to study the kinetics is to fit the time dependent reacted fraction ($\alpha$) to various analytical rate expressions, through which reaction mechanism and intrinsic rate limiting steps are determined [27].

The rate equation for the kinetics of solid-gas reaction is expressed as follows:

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

Where, $\alpha$ 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($\alpha$), i.e.

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

Based on experimental data of hydrogen absorption curve, the reacted fraction, $\alpha$ can be calculated as follow:

$$\alpha = \frac{p_0 - p_t}{p_0 - p_{eq}}$$

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 $g(\alpha)$ giving the best linearity with time is considered as the mechanism for hydrogen absorption in Ta-Al alloys. The rate function of hydrogen
absorption and the kinetic parameters $k$ are obtained from the linear regression fitting. The apparent activation energy for hydrogen absorption in these alloys is calculated using the Arrhenius equation

$$k = \frac{A e^{-E_a/RT}}{2}$$

or

$$\ln k = \ln A - \frac{E_a}{RT}$$

Where, $A$ is the pre-exponential factor, $R$ is the molar gas constant (J/mol K), $T$ is the process temperature (K) and $E_a$ is the apparent activation energy of the process (kJ/mol).

When rate constants at different temperatures are extracted from hydrogen absorption curves for Ta-alloys, the $E_a$ for hydrogen absorption can be obtained from the slope of ln$k$ vs 1/T plots. The apparent activation energy for the absorption of hydrogen by tantalum is increasing with increase in the alloying content in tantalum.

**Direction for Future Work, Summary and Conclusions**

**Direction for Future Work**

Tantalum is considered as a potential candidate material for hydrogen separation membrane functioning in a flowing gas at high temperature and high pressure for the separation of hydrogen from a mixture of gases. In the present thesis, the investigation is carried out on the solubility of hydrogen in various tantalum alloys with nickel, chromium, iron and aluminium at different compositions.

To evaluate the use of tantalum alloys for membranes for hydrogen permeation, further investigations are also required. These are on direct experimental determination of permeability, evaluation of mechanical properties of tantalum alloys before and after
hydrogen loading, as a function of temperature. Finally, the use of tantalum and tantalum alloys membranes in actual devices for hydrogen separation.

**Summary & Conclusions**

- Vacuum arc melting is a suitable technique for the preparation of homogeneous tantalum alloys with nickel, chromium, iron and aluminium.

- The solubility of hydrogen in tantalum and its alloys is obeying the Sievert’s law in the considered temperature range (673 K-873 K) and it is decreasing on the addition of nickel, chromium, iron and aluminium as alloying elements.

- The decrease in solubility may be attributed to increase in lattice strain energy and due to increase in e/a ratio. The decrease in lattice parameter of tantalum on the addition of alloying elements decreases the size of interstitial sites and hence, hydrogen solubility.

- The solubility of hydrogen in tantalum and tantalum-alloys increases with increase of hydrogen pressure but the solubility decreases with increase in temperature. This is also reflected by exothermic solution of hydrogen in all these samples.

- The relative change in enthalpy for the solution of hydrogen in tantalum increases with increase in concentration of these alloying elements whereas entropies values are nearly constant.

- The $\Delta H_{II}$ and $\Delta S_{II}$ values are constant in the considered temperature range (673 K - 873 K) and virtually independent of dissolved hydrogen concentration (0.367 wt % - 0.068 wt %).
The apparent activation energy for the solution of hydrogen in tantalum is increasing on the addition of aluminium as alloying elements in tantalum.

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