

THE EFFECT OF IRON ON THE SOLUBILITY BEHAVIOR OF HYDROGEN IN TANTALUM

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ABSTRACT

The separation, storage and recovery of hydrogen are key requirements for the efficient development of advanced hydrogen fuel technologies. The ideal hydrogen separation membrane should have high hydrogen permeability and good mechanical properties at a range of temperatures and pressures. Tantalum is a potential candidate with highest permeability to hydrogen among pure materials for hydrogen separation membrane. Isothermal as well as isobaric PCT equilibrium studies have been done in the temperature range of 673 – 873 K and hydrogen pressure range of 0.60 – 1.20 atmospheres for pure Ta and its solid solution alloys with Fe in different compositions. Results are presented.

1 INTRODUCTION

In view of the global warming and depletion of fossil fuels, the coexistence of environment safety and energy supply is said to be a major goal for the modern society of the 21st century [1-7]. Hydrogen has emerged as a technologically amenable, renewable and eco-friendly energy carrier that can be produced easily in large amounts and in a manageable time scale [1-2, 5, 7-14]. In this situation, the separation, storage and recovery of hydrogen are basic requirements for the efficient development of hydrogen fuel technologies [7-8, 15]. Hydrogen separation techniques also find applications in chemical, petrochemical, microelectronic industries, fuel cells and “Vision 21” program of DOE [5,16-18]. Production of hydrogen from gasified coal can be achieved via the water-gas-shift reaction, resulting in a stream consisting mainly of H₂ and CO₂ that would require separation [19]. This is creating a persistent interest in developing economically feasible methods for hydrogen separation [16-17]. The rapid development of membrane reactors and fuel cells has witnessed increasing interest in dense composite membranes for hydrogen separation and purification [20-21]. The ideal hydrogen separation membrane should have high hydrogen permeability and good mechanical properties at a range of temperatures and pressures.

Tantalum is a promising material as a component in hydrogen separation membranes operating at a range of temperature and a range of pressure [17, 21-22]. Its permeability to hydrogen is among the highest of any pure material and also has high hydrogen solubility [17, 22-24]. Ta is cheaper than Pd and its hydrogen permeability is significantly greater than Pd and Pd based alloys [5, 17, 24-26]. However, hydrogen embrittlement and surface oxidation are two main factors which have prevented the tantalum metal to be recognized it as permeable membranes [17-18, 21, 24, 26-30]. Surface oxidation of Ta can be minimized by coating with Pd [18, 31]. Hydrogen embrittlement problem arises from the change of lattice parameter or formation of hydrides mainly at low temperature below about 334K [31]. Therefore, the management of hydrogen solubility could be thought of as an approach to preserve the mechanical properties of the membrane while retaining its functional characteristics [29, 32]. The effect of Fe, Al, Ni, Cr, Mo, Cu, Pd, and Sn on the solubility and permeability act of group V elements has been widely studied [13, 18, 29, 32-40]. In all of these alloys, the experimentally measured solubility and permeability have been found to be inferior to that of pure metal. Importantly, however, the resistance to embrittlement and durability of these alloys are much better than the pure metal, while the permeability is still greater than the leading palladium alloys [26]. In order to develop the tantalum alloys as materials to meet the expected operating condition of a superior hydrogen separation membrane, it is essential that a broad and

sound body of theoretical and experimental information on the solubility and diffusivity behavior of hydrogen in these alloys should be established. No experimental data exists for the effect of iron on the solubility of hydrogen in tantalum. The present work aims to evaluate the effect of iron as an alloying element on the solubility of hydrogen in bcc Ta.

2 EXPERIMENTAL

The tantalum-iron (1.6 and 3.2 atom % Fe) alloys were prepared using high purity (> 99%), Aldrich make tantalum and iron foils in a stoichiometric weight ratio by using an arc melting technique in an argon atmosphere. The melting was repeated 6-8 times to make the alloys homogeneous. The alloys obtained in button form were cold rolled to 0.4 mm thickness and then cleaned with acetone. Elemental analysis of all the samples were carried out by using Glow Discharge – Quadrupole mass Spectrometry (GD-QMS) and the detailed chemical composition of the samples is shown in Table 1.

Table 1. Chemical composition of Ta-Fe alloys

Alloys (atom %)	Fe (atom %)	O (atom %)	N (atom %)	C (atom %)
Ta	-	0.7	0.06	.03
Ta-1.6Fe	1.6	0.75	0.05	.03
Ta-3.2Fe	3.2	0.77	0.06	.02

Phase characterization of the alloys was done by X-ray diffraction (XRD) (model: Inel make MPD) with Cr-K α radiation at 30 mA and 40 kV using a curved position-sensitive detector, thus the diffraction data in complete 2θ range was observed. Scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) spectroscopy—including X-ray dot mapping were performed to characterize the phase structure and the alloying element distribution. The specimens for hydrogen charging were cut into $0.4 \times 10 \times 15 \text{ mm}^3$ 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 mechanically polished on emery papers followed by cleaning with acetone. Hydrogen charging was carried out in a Sievert's apparatus [27] using 6N pure hydrogen gas. The hydrogen generator was used as a source for (99.9999 %) pure hydrogen gas from which required amount of hydrogen can be released and then disconnected from the system.

Sample was weighed and inserted in to the quartz sample holder which was further kept in the reaction chamber. A high vacuum of the order of 10^{-6} torr was created in the system using rotary and diffusion pump. The sample was heated at 1183 K under dynamic vacuum conditions for 2 hours to activate the sample surface. Hydrogen gas was flushed out through the system at temperature 1183 K and then system was evacuated again. The sample was then cooled up to required temperature. Hydrogen gas was introduced in to the system in the temperature range of 673 – 873 K and in the hydrogen pressure range of 0.60-1.20 atmospheres. The amount of hydrogen absorbed by the sample was monitored by the system pressure drop. A constant pressure reading up to 24 hrs ensured that equilibrium has been achieved in the system. The furnace was switched off and removed away from the reaction chamber and the valve connecting the sample holder to the remaining system was closed. The reaction chamber was rapidly cooled by quenching so that hydrogen absorption during cooling could be minimized and sample was taken out from the chamber. The amounts of hydrogen absorbed by the samples were analyzed by pressure drop method as well as by the inert gas fusion technique. Results from both methods were in good agreement. The hydrogen solubility of pure tantalum was compared with the solubility of hydrogen in different Ta-Fe alloys and different in solubility behavior on the addition of Fe was explained.

3 RESULTS

XRD pattern of Ta and Ta-Fe alloys before and after hydrogen charging is shown in Fig. 1. From XRD analysis, it is found that both the Ta-Fe alloys are bcc single phase i.e. solid solution of tantalum. Amount of hydrogen dissolved in Ta within solid solubility limit at higher temperature form the hydrides corresponding to the room temperature which is shown in Fig.1.

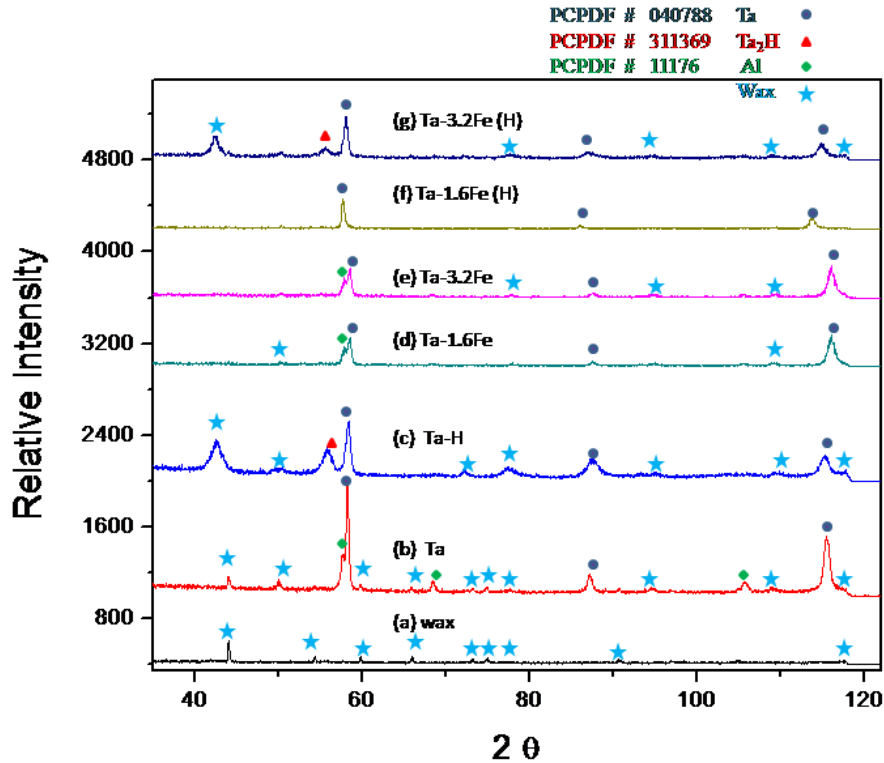


Figure 1. XRD pattern of Ta and Ta-Fe alloys before and after hydrogen charging

Scanning Electron Microscopy (SEM) and EDX analysis of Ta-3.2Fe alloy is shown in Fig. 2 which indicates that alloy is homogeneous and no other phase formation is occurred in Ta-Fe alloy.

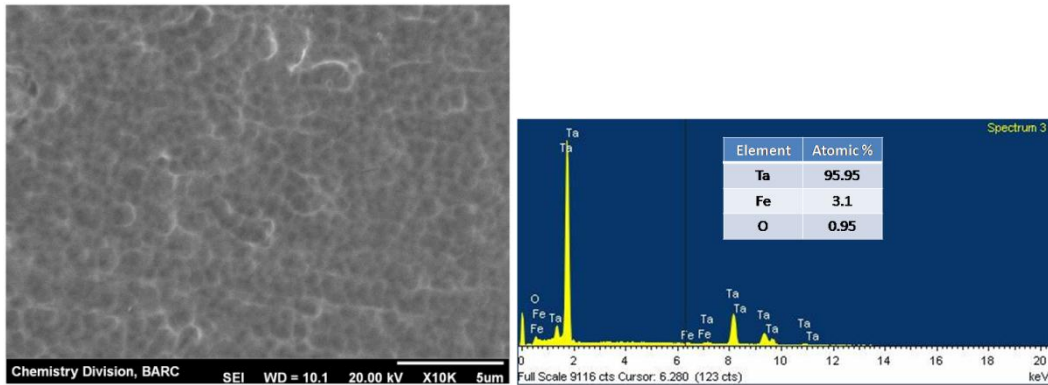


Figure 2. Scanning Electron Microscopy (SEM) and EDX of Ta-3.2Fe alloy

Ta-H phase diagram [41-44], shows that at temperature higher than 334 K, a single homogeneous α -phase exists in which metal atoms occupy a bcc lattice [45] and disordered hydrogen occupy tetrahedral sites of the bcc lattice [46-48]. The results of isothermal equilibrium P-C-T measurement for the Ta and its alloys with Fe are shown in Fig.3 and isobaric P-C-T curves are presented in Fig.4. Fig. 3 indicates that the hydrogen dissolved in the samples followed the Sievert's law which states that the dissolved hydrogen concentration (X) is proportional to the square root of pressure (\sqrt{p}). The square root dependence follows from the fact that hydrogen dissolves in atomic form in the host matrix [49-51]. Fig. 3 also indicates that solubility of hydrogen in Ta and Ta-Fe alloys decreases with increase in temperature but increases with increase of pressure. The increases in Fe content in Ta decreases the solubility of hydrogen as shown in Fig. 5.

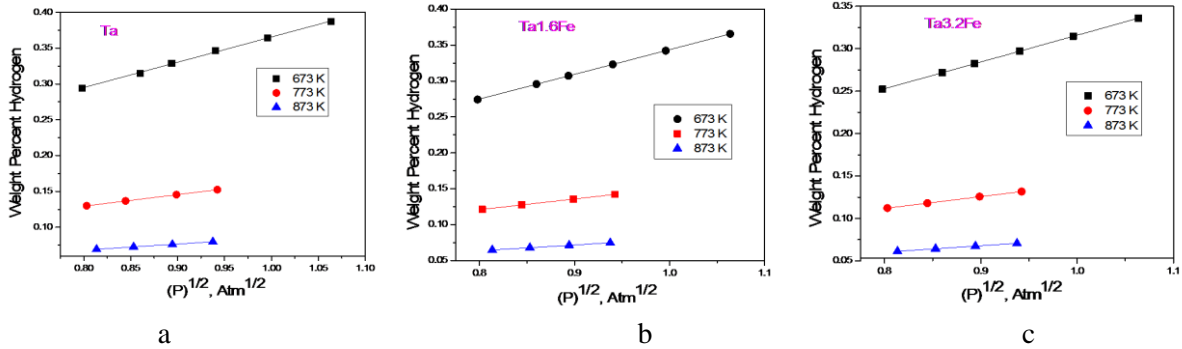


Figure 3. Variation of dissolved hydrogen concentrations with the square root of equilibrium hydrogen pressure at constant temperature for (a) Ta, (b) Ta-1.6Fe and (c) Ta-3.2Fe

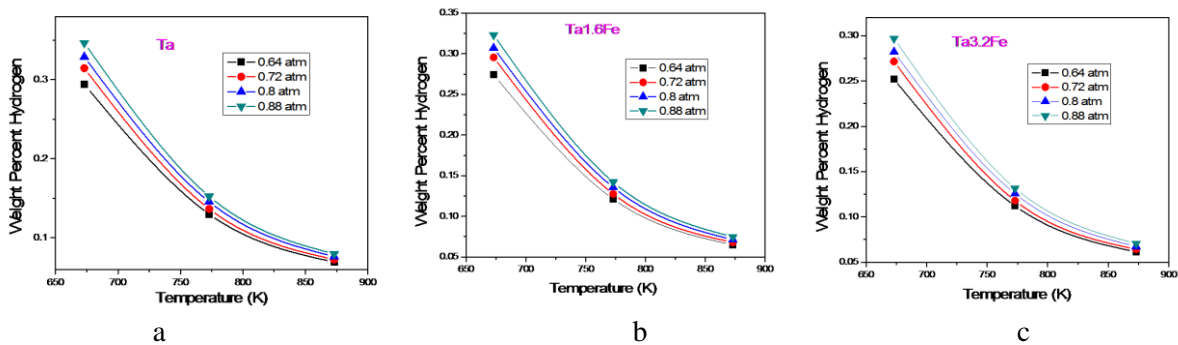
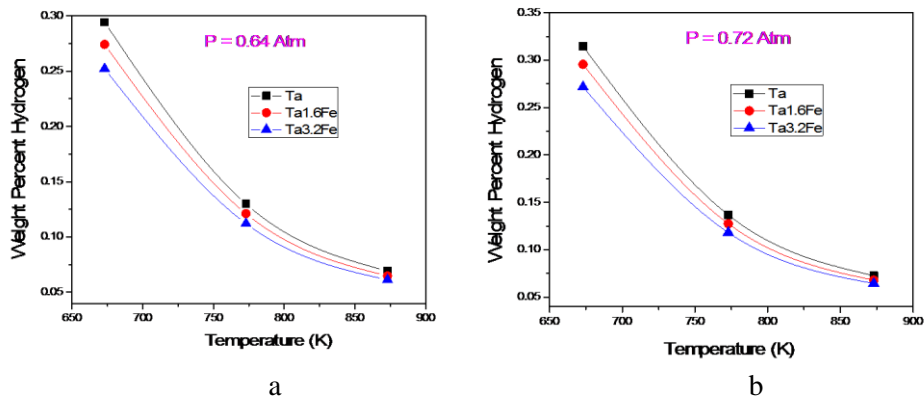


Figure 4. Variation of dissolved hydrogen concentrations with temperature at constant pressures for (a) Ta, (b) Ta-1.6Fe and (c) Ta-3.2Fe



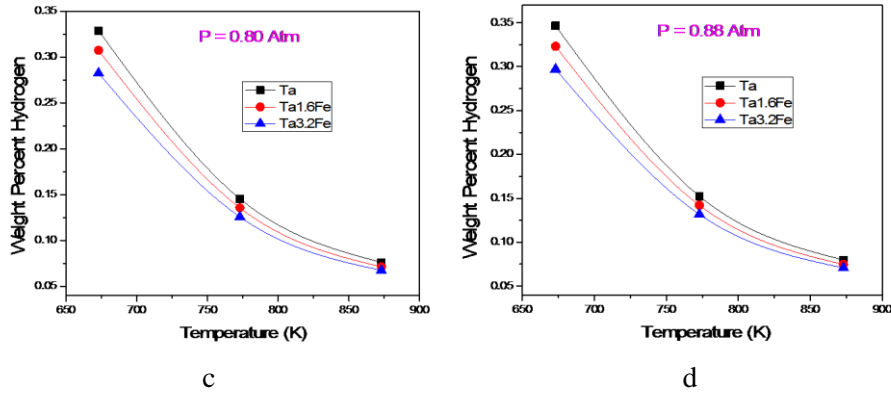


Figure 5. Isobaric PCT equilibrium curves showing the effect of Fe addition on the solubility of hydrogen in tantalum at (a) 0.64 Atm, (b) 0.72 Atm, (c) 0.8 Atm and (d) 0.88 Atm

4 DISCUSSIONS

The decrease in solubility of hydrogen in tantalum with increase in Fe content is explained on the basis of repulsive interaction between H and Fe atoms. An interaction of interstitial and substitutional atoms is considered to be mainly caused by change in electronic structure and the change in strain energy of dissolved hydrogen due to presence of interstitial sites with different size around a substitutional atom [36]. The difference between the atomic radii of solvent and substitutional atoms causes the difference in the size of interstitial sites. Makrides [52] has interpreted the increase of hydrogen solubility in Pd-Ag alloys is due to an attractive interaction between H and Ag atoms. Further, Brodowsky [53] has interpreted that addition of Ag in Pd causes the lattice expansion and hence the lattice strain energy resulting from dissolved hydrogen is lower in Pd-Ag alloys as compared to pure Pd. Wagner [54] has pointed out that increase of hydrogen solubility in Pd-alloys is due to increase of lattice parameter of Pd on the addition of alloying element, and that interaction between H and Ag atoms in Pd-Ag-H alloys is not dominant [36].

According to Pauling [55], the atomic radii of Ta and Fe for metallic bond with a coordination number of eight are 145 and 140 pm respectively. The lattice parameter of Ta decreases with the addition of Fe atoms. Therefore the decrease of hydrogen solubility in Ta-Fe alloys can be explained by the increase in lattice strain energy as proposed by Brodowsky [53].

Other possible reasons for decrease in hydrogen solubility in Ta on the addition of Fe may be intrinsic effect [18]. Since Fe has much lower hydrogen solubility than pure Ta, therefore increase in numbers of Fe atoms could be expected to block the sites for hydrogen absorption in Ta-based lattice. The unavoidable formation of iron oxides during arc melting may reduce the effective surface area for hydrogen absorption in the lattice and act as a most effective barrier for hydrogen absorption [18].

It is also observed that enhancement in e/a ratio results in decreasing the hydrogen solubility in the main matrix [13, 51]. For example, the addition of Mo (electronic configuration $4d^35s^1$) to Nb (electronic configuration $4d^45s^1$) increases the e/a ratio which results in reduction in hydrogen solubility in Nb-Mo alloys with the addition of Mo content [38]. On the basis of the above argument, addition of Fe (electronic configuration $3d^64s^2$) in Ta (electronic configuration $5d^46s^1$) increases the e/a ratio and hence, decreases the solubility of hydrogen in tantalum.

5 CONCLUSIONS

The amount of hydrogen dissolved in Ta-Fe alloys has obeyed the Sievert's law. The hydrogen solubility in tantalum decreases with increase in Fe content. Moreover the interaction between Fe and H in the solid

solution seems to be repulsive. This may reflect in a reduction in the ability to take hydrogen in to solid solution of Ta-Fe, with increasing Fe content.

ACKNOWLEDGMENT

The authors are grateful to Dr. A.K. Suri, Director Materials Group, BARC and Dr. G.P. Tiwari for their continuous guidance during the manuscript preparation.

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