



The Effect of Iron on the Solubility Behavior of Hydrogen in Tantalum

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Presented by

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Why this study is carried out ?

❑ The limited availability of fossil fuels, increasing energy demand and the global warming has led to a search for the sources of clean, and renewable energy.

❑ Hydrogen is a clean, non-polluting, and renewable source of energy carrier considered for both mobile and stationary applications.

❑ The production, purification/separation, storage and recovery of hydrogen each represent a significant technological barrier delaying the use of hydrogen energy.

❑ Apart from the proposed hydrogen economy, there is already a major demand for hydrogen in the development of industries like metallurgical, chemical, petrochemical, microelectronic, textile, pharmaceutical, and fuel cells. Thus hydrogen separation technology has become increasingly important [02Zha].

❑ Hence, a cost-effective and proficient means to hydrogen purification will always be a necessity and this is creating a persistent interest in developing economically feasible methods for the hydrogen separation.

❑ Also, In gasifier, where water-gas-shift reaction occurs and resulting in a stream consisting mainly of hydrogen and CO_2 , hydrogen separation is required [03Rot].

❑ Hence, the ideal hydrogen separation membrane should have high hydrogen permeability and good mechanical properties [03Hara] to endure the pressure difference between upstream and downstream side, high temperature, and to be resistance to hydrogen embrittlement.

❑ The performance of the membrane depends on permeability of hydrogen through it. The permeability, in turn, depends on the solubility of hydrogen and the diffusion coefficient of hydrogen in the metal.

❑ Tantalum is considered as a potential candidate material for the hydrogen separation membrane operating in a flowing gas at high temperature and high pressure for the separation of hydrogen from a mixture of gases [03Rot].

□ Tantalum has higher hydrogen solubility and larger diffusion coefficient.

$$S(\text{H}_2/\text{Ta}) = 0.132 \exp(4050/T) \text{ mol/m}^3 \cdot \text{Pa}^{1/2}$$

$$D(\text{H}_2/\text{Ta}) = 4.4 \times 10^{-8} \exp(-1620/T) \text{ m}^2/\text{s}$$

$$\phi(\text{H}_2/\text{Ta}) = 5.8 \times 10^{-9} \exp(2430/T) \text{ mol/m} \cdot \text{s} \cdot \text{Pa}^{1/2}$$

□ It is mechanically tough and durable material that can be easily included into metal infrastructure in a range of temperature [03Rot].

□ It is cheaper and possesses about order of magnitude larger hydrogen permeability than the well known hydrogen permeable membrane made up of Pd alloys.

Why Fe is added as an alloying element in Ta ?

❑ High hydrogen solubility of tantalum causes the hydrogen embrittlement problem arises from the hydride formation or change in lattice parameter and this is the main limitation of tantalum metal to be commercially recognised it as a hydrogen separation membrane [72Owen].

❑ It was observed that for a given thermodynamic condition, reducing the hydrogen solubility by the addition of alloying element could be thought as an approach to preserve mechanical properties of the hydrogen separation/permeable membrane [12Kim].

❑ The influence of iron as an alloying element on the solubility of hydrogen in vanadium has been reported in the literature (same group element as that of Ta). It was observed that addition of Fe in vanadium reduces the hydrogen solubility. Moreover, the vanadium hydrides become unstable on the addition of Fe in V [03Yuk].

❑ Hence, to find out the effect of iron on the solubility behavior of hydrogen in tantalum, iron is added as an alloying element in Ta.

Objective of the study

- ❑ To investigate the isothermal as well as isobaric pressure-composition-temperature (PCT) equilibrium measurements for the solubility of hydrogen in Ta and Ta-Fe alloys.
- ❑ To investigate the effect of iron as an alloying elements on the solubility of hydrogen in tantalum.
- ❑ To calculate the thermodynamics parameters, the relative change in enthalpy, entropy and Gibb's free energy for the solution of hydrogen in the Ta and Ta-Fe alloys from equilibrium PCT measurements. As per our knowledge, the solubility data and thermodynamic parameters for the Ta-Fe alloys have not been previously reported in the literature.

Experimental

Preparation of Ta-alloys:

- Ta - (1.6 and 3.2 at % Fe) alloys were prepared by using arc melting technique in an inert atmosphere.
- The melting was repeated 6-10 times to make the alloys homogeneous.
- The homogeneity of the alloys was ensured by measuring Vickers Hardness of the alloys and by line scan SEM-EDX analysis.
- The alloys obtained in button form were cold rolled up to 0.3 mm thickness and then cleaned with acetone and cut it into small pieces of dimension $0.3 \times 10 \times 15 \text{ mm}^3$.
- Before hydrogen incorporation, all the samples were cleaned chemically using an acidic solution ($\text{HF}:\text{HNO}_3:\text{H}_2\text{SO}_4::2:2:5$) and mechanically polished on emery papers followed by cleaning with acetone.

Equipment Used for Equilibrium Hydrogen Charging

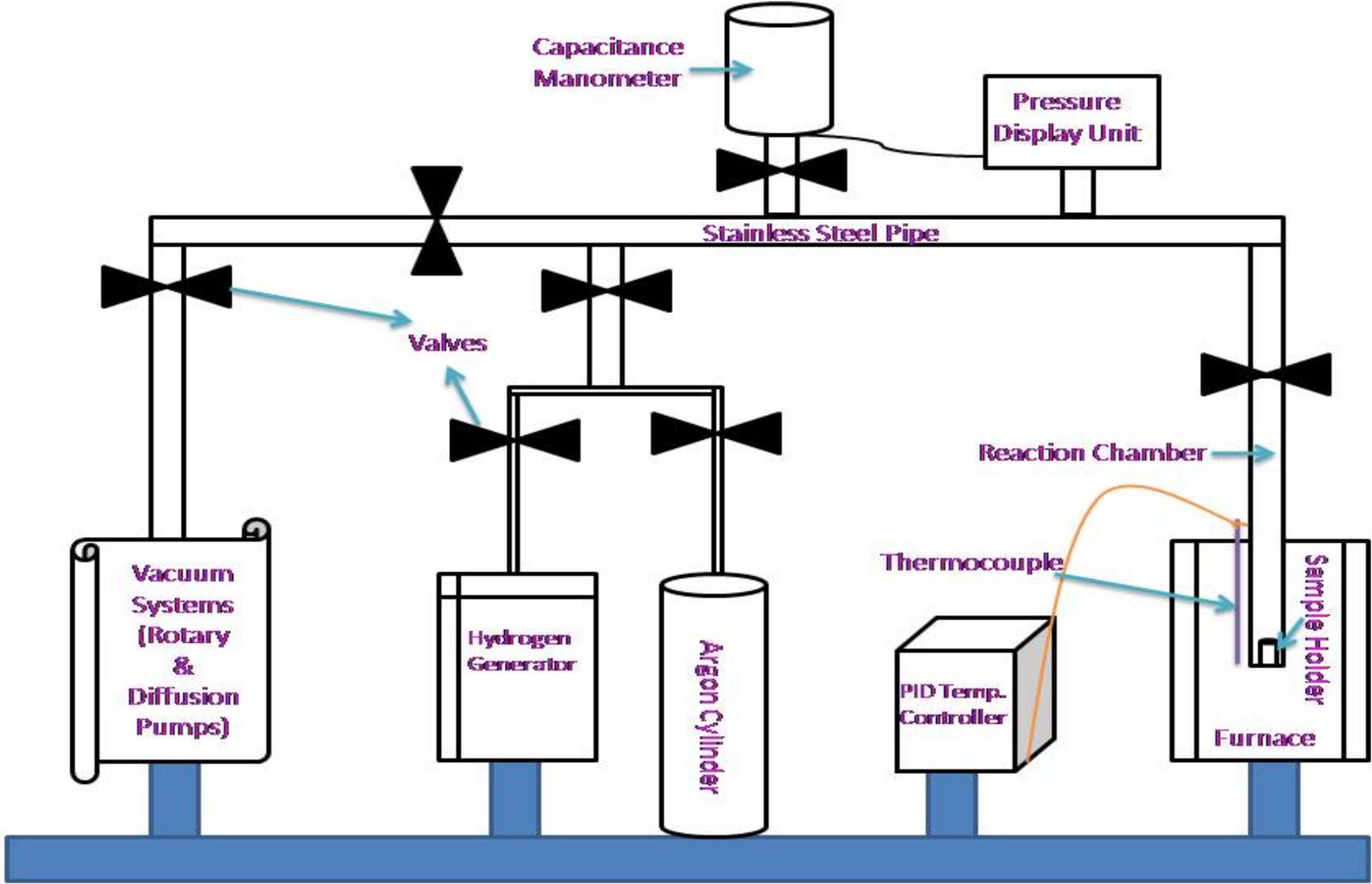


Fig.1. Block Diagram of Seivert's Apparatus Used for Hydrogen Charging

Procedure for hydrogen charging

- ❑ Sample was weighted and inserted 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 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.
- ❑ To obtain isothermal PCT curves, hydrogen gas was introduced into the system from the hydrogen generator at a constant temperature and at a particular 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. 9

- 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.
- Then furnace was switched off and removed it away from the reaction chamber and the valve connecting the sample holder to the remaining system was disconnected. The hydrogen gas present inside system was replaced by Argon gas. 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 pressure drop method as well as by inert gas fusion technique.

Results and discussion

Vickers hardness for each sample was measured at 10 – 13 different points. Uniform readings observed within $\pm 5\%$ variation in all the samples indicates the homogeneity of the alloys and these values are shown in Table 1 .

Table 1

Alloys (Atomic %)	Vickers Hardness (HV)
Ta	230 \pm 3 %
Ta1.6Fe	268 \pm 5 %
Ta3.2Fe	303 \pm 4 %

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

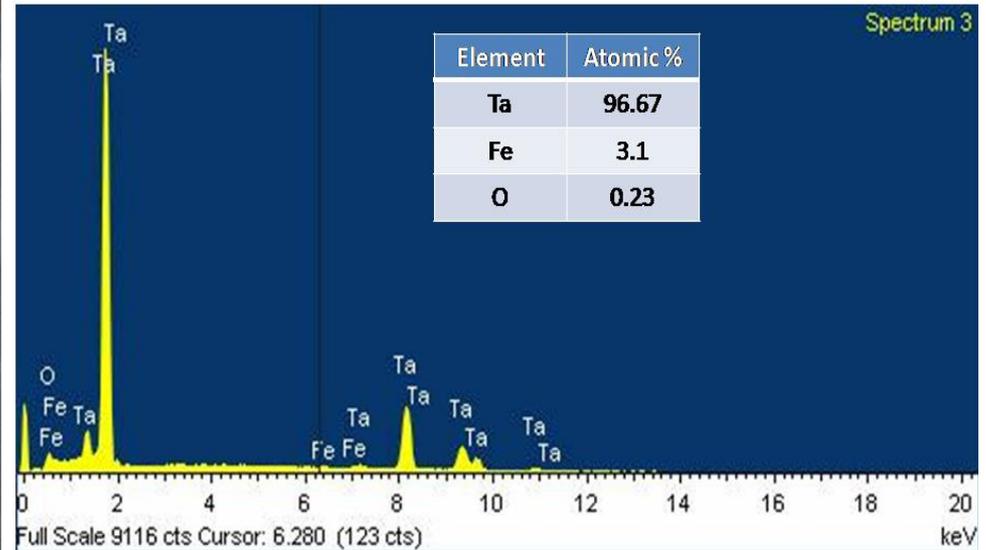
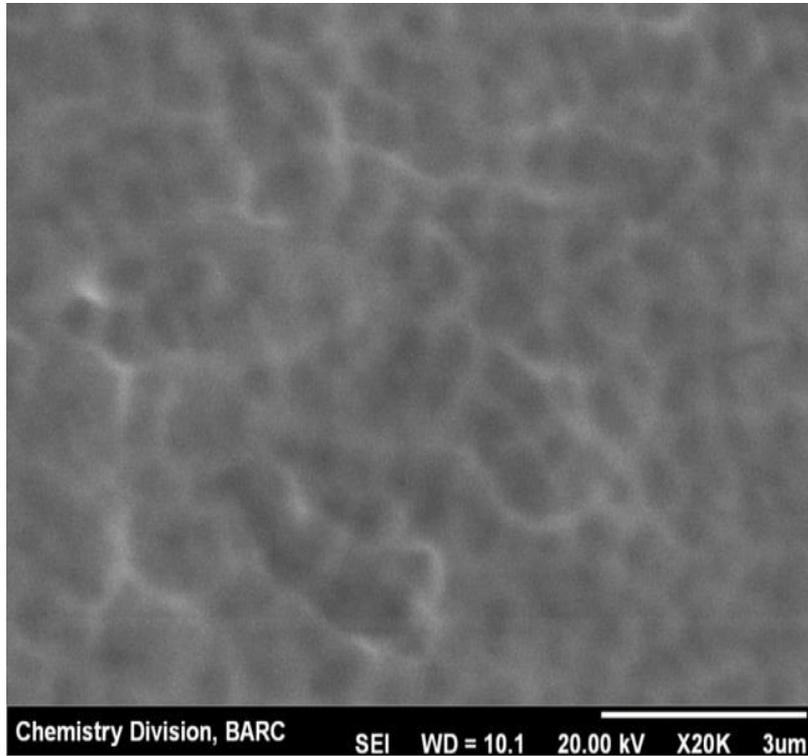


Fig. 2 (a)

Fig. 2 (b)

The detailed chemical compositions of the samples analyzed by using GD-QMS are shown in Table 2.

Table 2

Alloys (atom %)	Fe (atom %)	O (atom %)	N (atom %)	C (atom %)
Ta	-	0.10	0.06	0.03
Ta-1.5Fe	1.6	0.22	0.02	0.03
Ta-3.0Fe	3.2	0.23	0.06	0.02

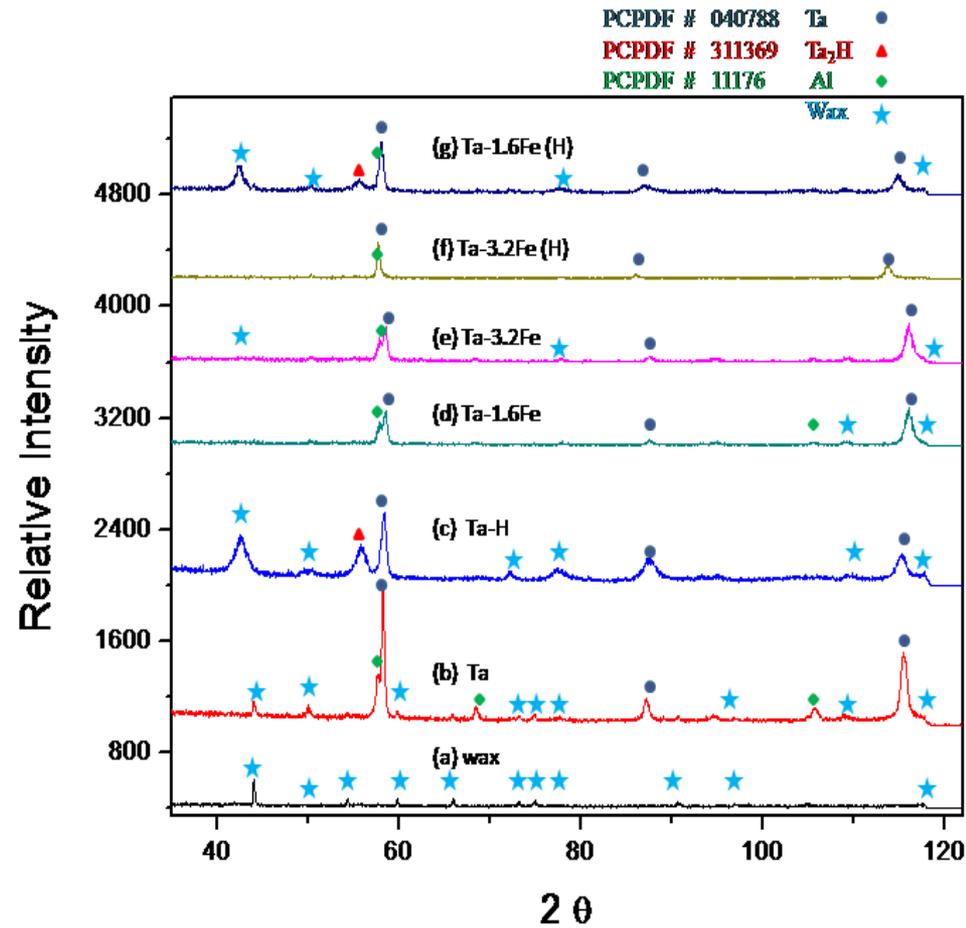
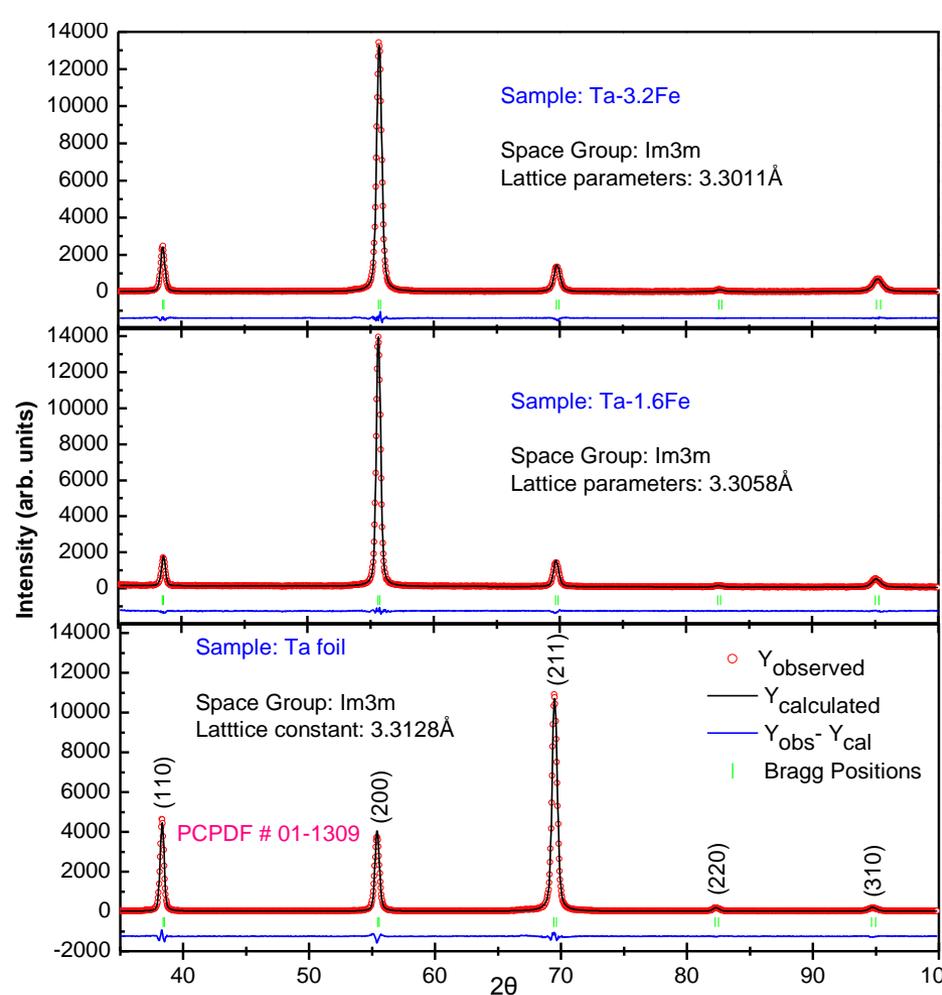


Fig. 3 XRD pattern of Ta and Ta-Fe alloys

After hydrogen charging, a tantalum hydride phase is observed in case of Ta and Ta-1.6Fe but no hydride phase is observed in case of Ta-3.2Fe alloy

From the phase diagram of Ta-H system, it is clear that above 334 K, there is no hydride phase. Above this temperature, (α Ta) is in equilibrium with (α Ta) + H₂.

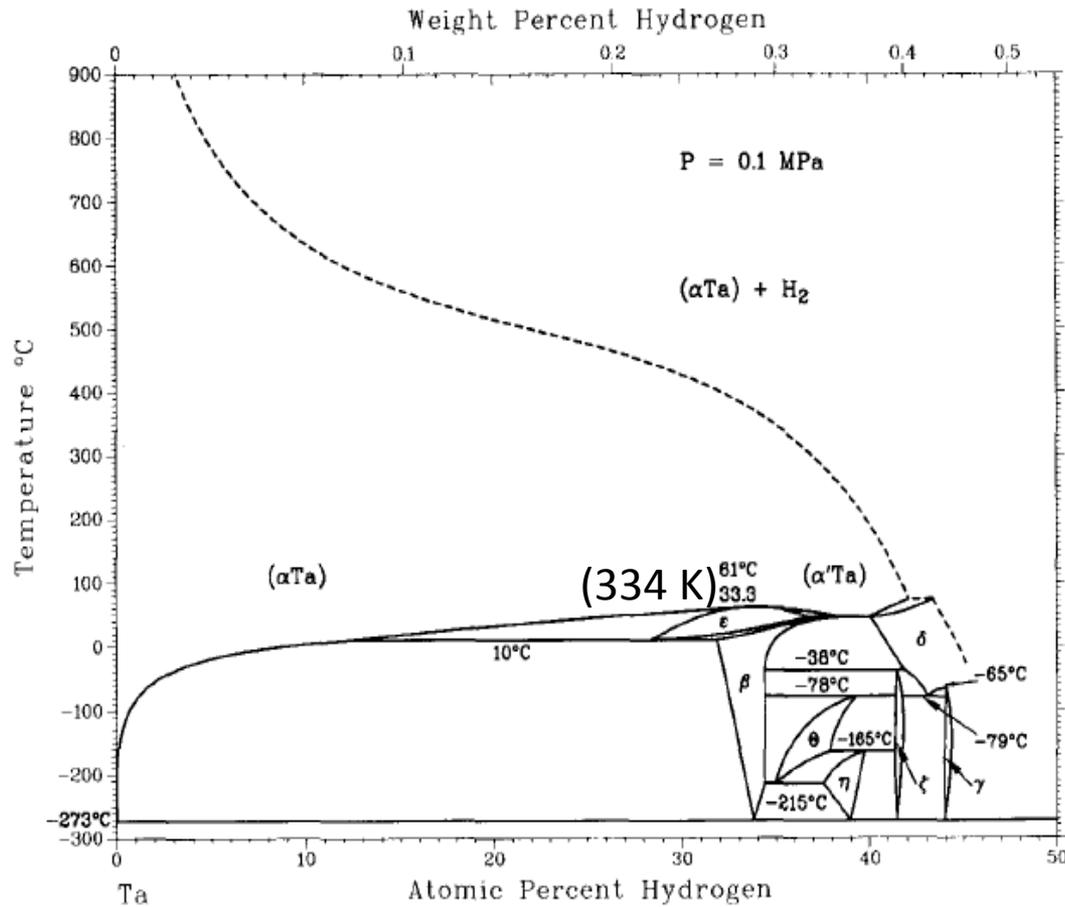


Fig.4 By A. San. Martin and F.D. Manchester et.al.

□ In the present work, P-C-T equilibrium measurements have been investigated in the temperature range of 673 – 873 K, and it is observed that the amount of dissolved hydrogen is within the solid solubility limit and follows the **Sievert's law** which states that

$$c \propto \sqrt{p} \quad (1)$$

$$\text{or } c = K_s \sqrt{p} \quad (2)$$

where c = amount of dissolved hydrogen

p = Hydrogen Gas Pressure

K_s = Sievert's Constant

□ The square root dependence follows from the fact that hydrogen dissolves in atomic form in the host matrix .

□ The change in hydrogen concentration with respect to alloying element content in Ta metal is shown in Fig. 5.

□ The isothermal as well as isobaric curves showing the effects of Fe addition are shown in Fig.6 and Fig.7, respectively, at three different temperatures and at four different pressures which indicate that solubility of hydrogen in Ta decreases on the addition of the iron as alloying elements.

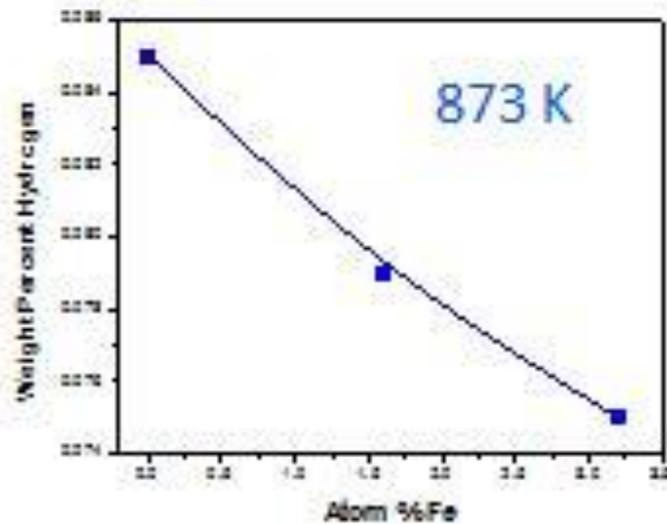
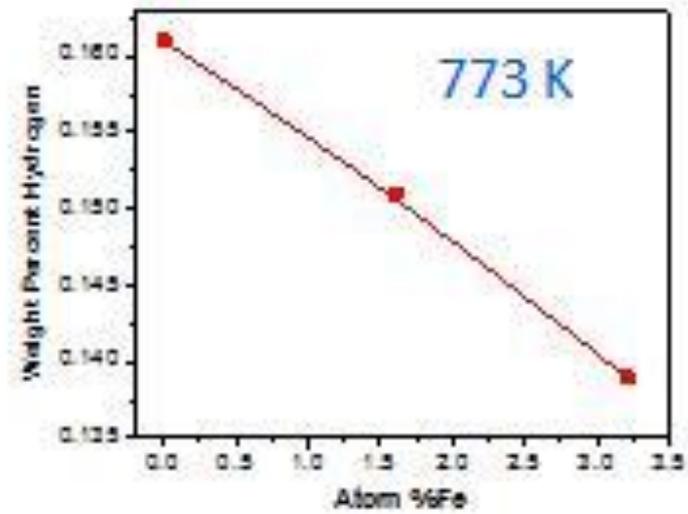
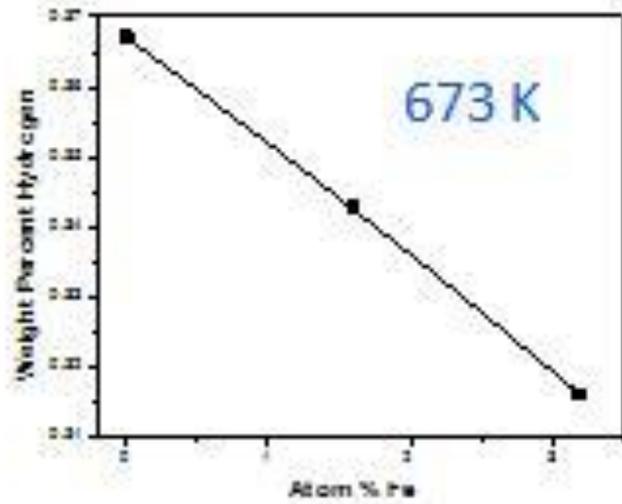


Fig.5 The variation of dissolved hydrogen (wt %) in Ta-Fe alloys w.r.t. Fe Concentration

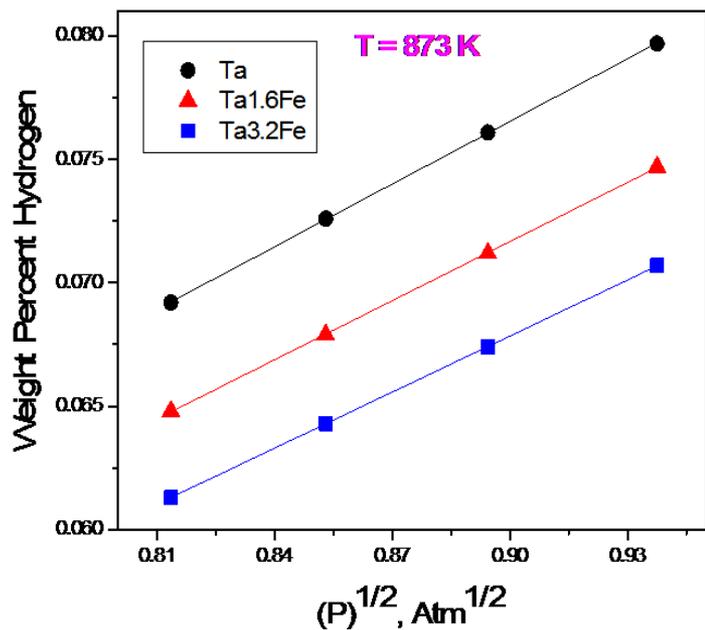
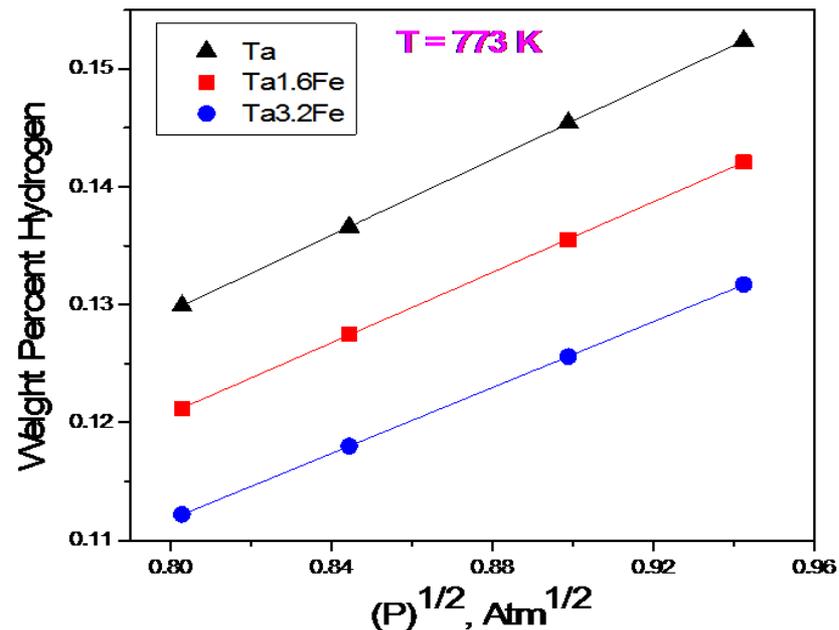
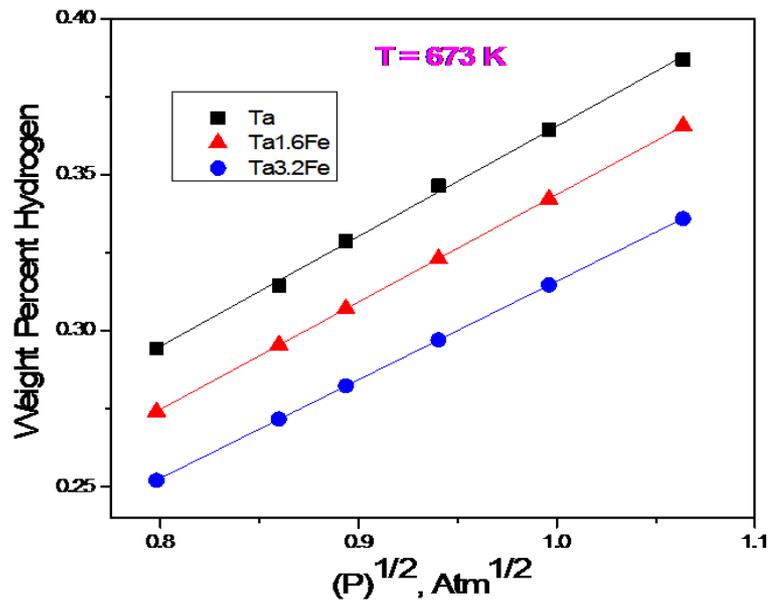


Fig.6 Isothermal PCT equilibrium curves at three different temperatures (a) 673 K, (b) 773 K and (c) 873 K

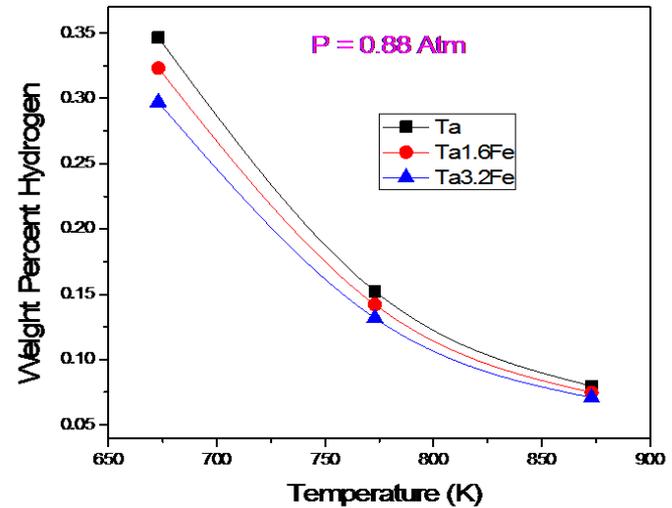
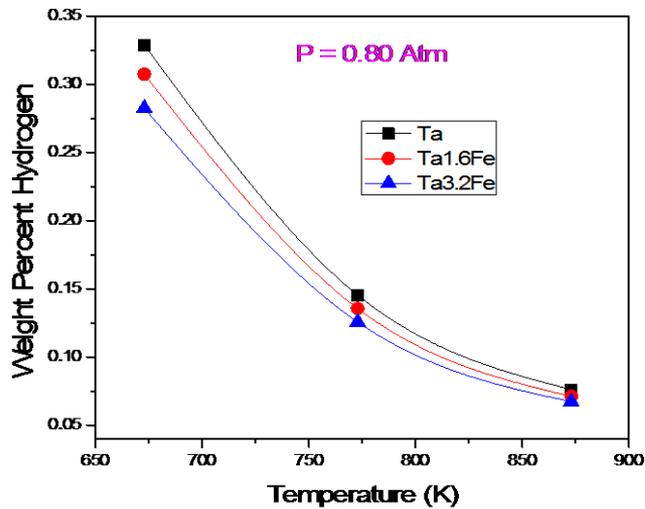
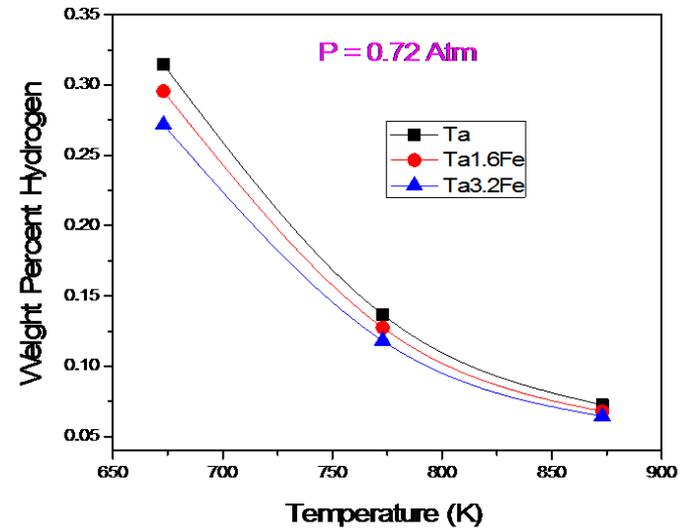
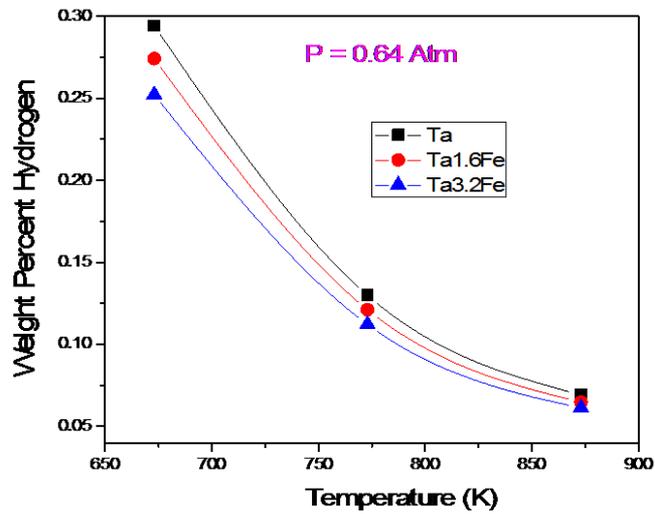


Fig.7 Isobaric PCT equilibrium curves at different hydrogen pressures (a) 0.64 atm (b) 0.72 atm (c) 0.80 atm and (d) 0.88 atm

The K_s values are calculated using Sievert's law for the solubility of hydrogen in Ta and Ta-Fe alloys at three different temperatures and at one atmosphere hydrogen pressure

Table 3 K_s , Sievert's constant for hydrogen in Ta and Ta-Fe alloys

Sample (atom %)	$K_s, 10^{-2}$		
	673 K	773 K	873 K
Ta	36.8	16.1	8.5
Ta-1.6Fe	34.3	15.0	7.9
Ta-3.2Fe	31.5	13.9	7.5

The relative change in enthalpy and entropy for solution of hydrogen in Tantalum metal and its alloys are calculated using the Sievert's relation :

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

or

$$\log K_s = \log c/\sqrt{p} = -\overline{\Delta H_H}/4.575T + \overline{\Delta S_H}/4.575$$

From the slope and intercepts of the $\log K_s$ vs $1/T$ plots, the values of relative change in enthalpy and entropy of hydrogen solution are calculated respectively. The values for relative change in Gibb's free energy are also calculated at different temperatures using these values.

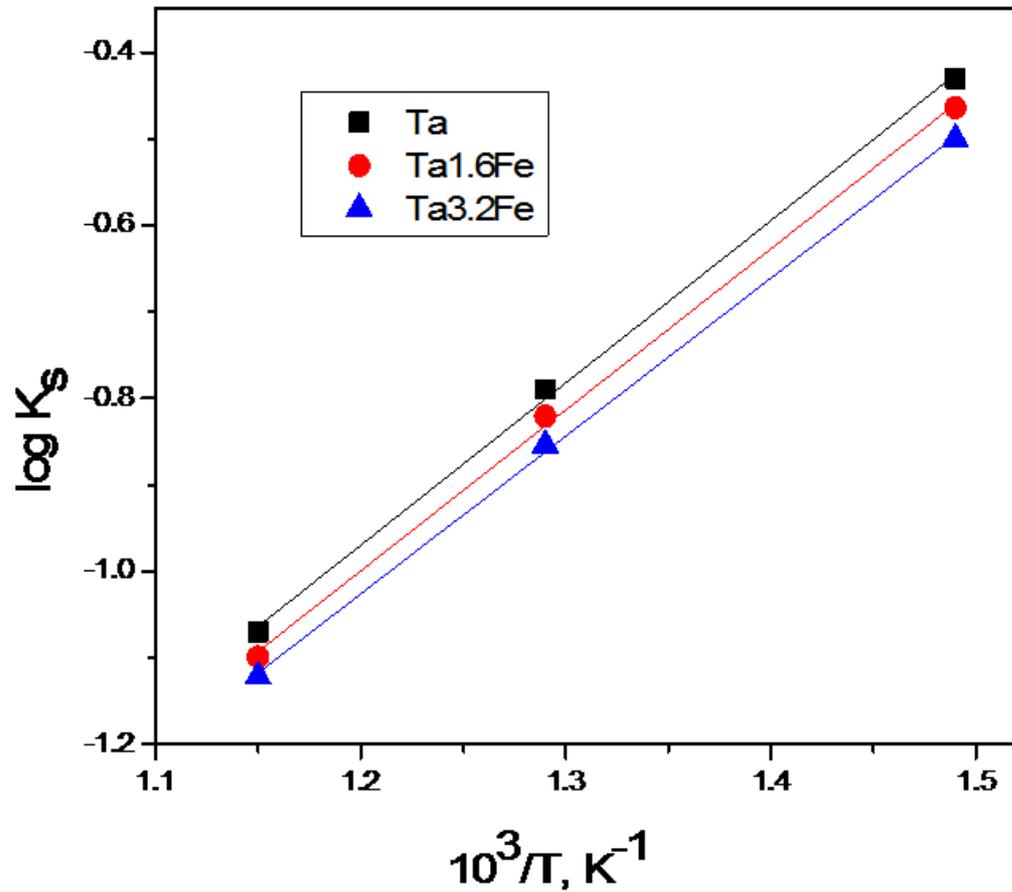


Fig. 8 Plot of $\log K_s$ vs $10^3/T$ (K) for the of Ta-H system and Ta-Fe-H systems

Table 4(* represent the values from literature)

Sample (atom %)	$\overline{\Delta H_H}$ (cal/g atom H)	$\overline{\Delta S_H}$ (cal/K/g atom H)	Temperature range (K)
Ta	- 8580 ± 250	- 14.7 ± 0.3	673-873
Ta-1.6Fe	- 8460 ± 160	- 14.7 ± 0.1	673-873
Ta-3.2Fe	- 8320 ± 220	- 14.6 ± 0.2	673-873
Ta*	- 7700 ± 100	-	703-717 [74Kle,78Dan, 96Sch]
Ta*	- 9400 ± 100	- 13.3 ± 0.2	195 -513 [71Pry]
Ta*	- 8850 ± 350	- 12.6 ± 2	573-773 [62Mal]

Table 5 (* represent the values from literature)

Temperature (K)	$\overline{\Delta G_H}$ (cal/g atom H)		
	Ta (H)	Ta-1.6Fe (H)	Ta-3.2Fe (H)
673	1330	1430	1510
723	2060	2160	2240
773	2800	2890	2970
823	3540	3630	3700
873	4270	4360	4430
917* [77Fra]	4390		
973* [77Fra]	5100		
1023* [77Fra]	5760		

Possible causes responsible for change in hydrogen solubility:

□ The change in strain energy of dissolved hydrogen due to presence of different size interstitial sites around a substitutional atom may be responsible for change in hydrogen solubility and it may be attributed to repulsive interaction between H and Fe atoms [75Mat].

□ The decrease of hydrogen solubility in Ta-Fe alloys could be explained due to increase in lattice strain energy as proposed by Brodowsky [72Bro]. The atomic radii of Ta and Fe are 146 and 126 pm respectively, at Pauling scale [45Pau]. The lattice parameter of Ta alloys decreases with the addition of Fe atoms. Moreover, the decrease in lattice parameter of Ta on the addition of Fe is also observed experimentally and seen clearly from the XRD pattern (Fig. 3). Therefore, the lattice size and interstitial sites size decrease and hence solubility decrease.

Table 6 Variation in H-solubility with respect to change in lattice parameter

Element	Lattice constant (before H-charging) (Based on Le Bail fitting of XRD data)	H-Solubility (wt % \pm 1 %)
Ta	3.3128 \pm 0.0004	0.367
Ta-1.6Fe	3.3058 \pm 0.0003	0.343
Ta-3.2Fe	3.3011 \pm 0.0002	0.316

Measurement were done on Bruker D8 Discover Diffractometer with Cu source with $K\alpha_1$ & $K\alpha_2$.

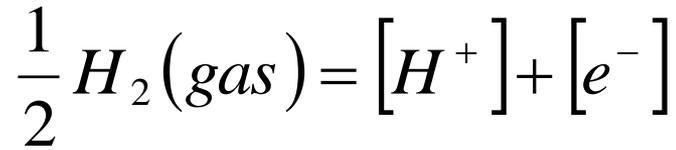
For accurate estimation of lattice parameters, Le Bail fitting was done using FullProf program. Set-up used was Bragg Brentano Geometry .

❑ The change in electronic structure may also be responsible for change in the hydrogen solubility.

❑ According to DFT theory, the calculated absorption energy of hydrogen shows greater dependency on electronic structure.

❑ 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.

❑ As the H_2 gas dissolves in the metal in the form of protons and electrons:



and at equilibrium condition,

$$\frac{1}{2} H_{H_2}^{(gas)} = \overline{H}_{H^+} + \overline{H}_{e^-}$$

Where \overline{H}_{H^+} and \overline{H}_{e^-} are the partial molar enthalpies of protons and electrons respectively in the metal.

Since the gas phase is ideal and the concentration of proton in the metallic phase is small, above Eq. can be rewritten as,

$$\frac{1}{2} H_{H_2}^0 + \frac{1}{2} RT \ln P_{H_2} = \overline{H}_{H^+}^* + RT \ln c + \overline{H}_{e^-}$$

Where $H_{H_2}^0$ is the molar enthalpy of hydrogen gas at 1 atmosphere pressure, c is the concentration of hydrogen in metal and $\overline{H}_{H^+}^*$ is the partial molar enthalpy of protons extrapolated to unity concentration. Solving above Eq. for c , we have [52Wag]

$$c = \sqrt{p_{H_2}} \exp \left[\frac{\frac{1}{2} H_{H_2}^0 - \overline{H}_{H^+}^* - \overline{H}_{e^-}}{RT} \right]$$

Hence, for a given hydrogen pressure, if partial molar enthalpy of electrons is increased on the addition of alloying elements, the concentration of dissolved hydrogen will decrease.

But in the present study, electron factor does not seem to be more important in case of Ta-Fe alloys.

As electronegativity of Ta is smaller than Fe and e/a ratio decrease with increasing concentration of Fe.

Table 7 Electronegativities of the elements (Pauling scale)

Element	Crystal Structure	Electronegativity
Ta	BCC	1.5
Fe	BCC	1.83

Table 7. Variation in H-solubility with respect to change in e/a ratio

Element	e/a Ratio	H-Solubility (wt %)
Ta	5	0.367
Ta-1.6Fe	4.952	0.343
Ta-3.2Fe	4.904	0.316

Here Oxidation state taken for Ta is +5 and for Fe is +2

Conclusion

- ❑ The solubility of hydrogen in Ta and Ta-Fe alloys is obeying the Sievert's law in the considered temperature range (673 K-873 K) and it is decreasing on the addition of Fe as an alloying element.
- ❑ This is attributed to increase in lattice strain energy
- ❑ The solubility of hydrogen in Ta and Ta-Fe alloys increases with increase of hydrogen pressure but decreases with increase in temperature.
- ❑ The relative change in enthalpy for the solution of hydrogen in tantalum increases with increase in concentration of iron as an alloying element whereas entropies values are nearly constant.
- ❑ The $\overline{\Delta H_H}$ and $\overline{\Delta S_H}$ values are almost independent of temperature in the studied temperature range (673-873) K and virtually independent of dissolved hydrogen concentration.

Significance of this study

□ The data can be used to process the design for Ta-based metallic hydrogen separation membranes and can also be utilized as valuable experimental information in various modeling studies for hydrogen solubility and permeability.

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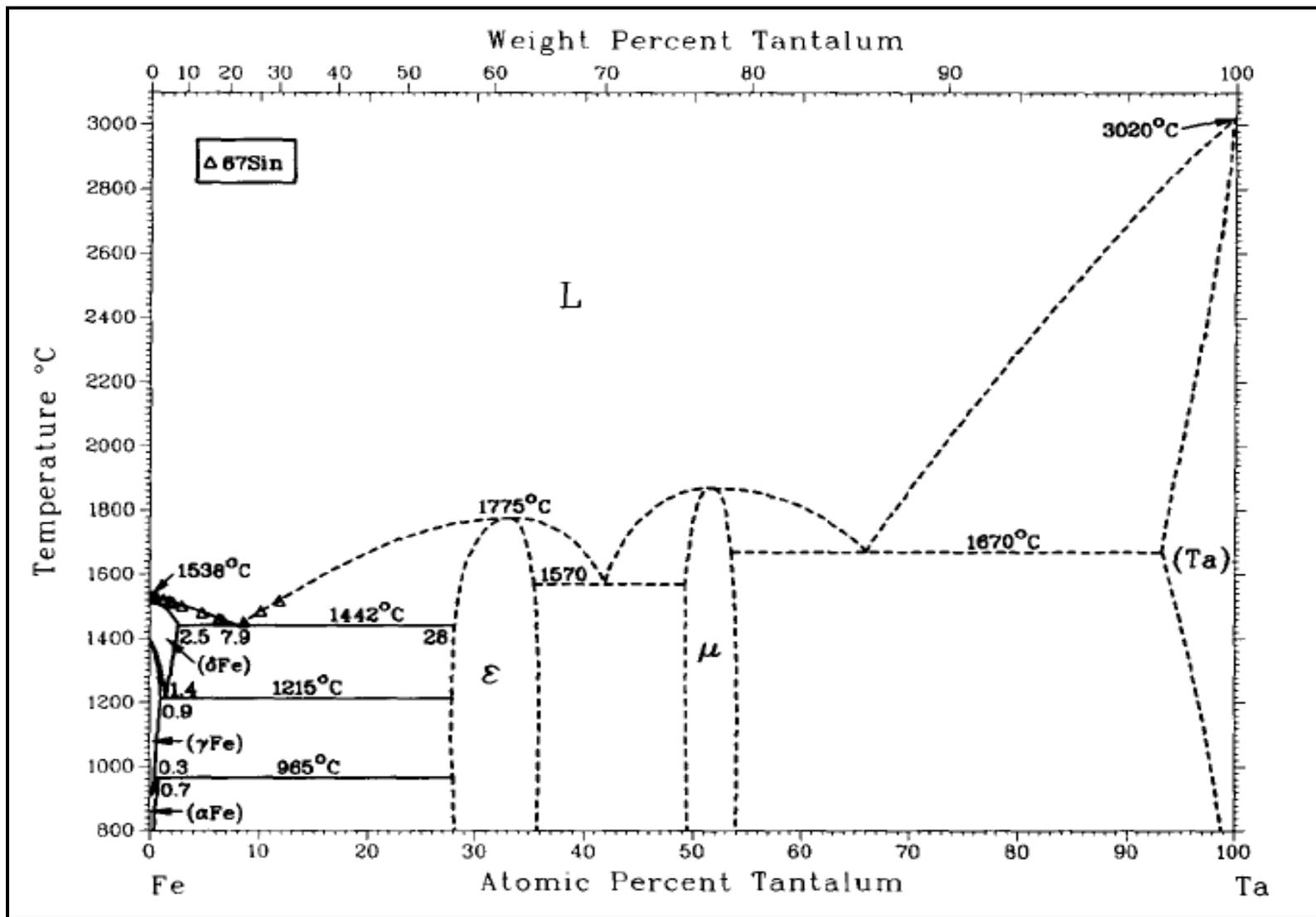
International Journals Publications

1. **Manju Taxak**, S. Kumar, N. Krishnamurthy, Thermodynamic Parameters for the Ta-Cr-H Solid Solution from Equilibrium P-C-T Data, J. Chem. Thermodyn. 63 (2013) 48-54.
2. **Manju Taxak**, S. Kumar, B. Kalekar, N. Krishnamurthy, Effect of nickel addition on the solubility of hydrogen in tantalum, Int. J. Hydrogen Energy, 38 (2013) 7561-7568.
3. **Manju Taxak**, S. Kumar, N. Krishnamurthy, A.K Suri, G.P.Tiwari, Change in lattice parameter of tantalum due to dissolves hydrogen, Int. J of Processing and Application of Ceramics **2012**, 6(2)73-76.
4. S. Kumar, A. Tirpude, **Manju Taxak**, N. Krishnamurthy, Hydrogen absorption kinetics in ball milled V + 80wt % LaNi₅ composite, Journal of alloys and compounds 2013, Accepted, In Press Ref. No. 2013 JALCOM-D-12-04562.
5. S. Kumar, **Manju Taxak**, N. Krishnamurthy Hydrogen absorption kinetics of V₄Cr₄Ti alloy prepared by aluminothermy process. Int. J. Hydrogen Energy 2012, 37(4) 3283-3291.

6. S. Kumar, **Manju Taxak**, N. Krishnamurthy A. K Suri and G.P Tiwari, Terminal solid solubility of hydrogen in V-Al solid solution, Int. J. of Refractory and Hard Materials 31, 2012, 76-81
7. S. Kumar, **Manju Taxak** and N. Krishnamurthy, Hydrogen absorption kinetics of V-Al alloy. J Thermal Analysis and Calorimetry; 112 (1) (2013) 5-10.
8. S. Kumar, **Manju Taxak** and N. Krishnamurthy, Synthesis and hydrogen absorption kinetics of V_4Ti_4Cr alloy. J Thermal Analysis and Calorimetry; 112 (1) (2013) 51-57.
9. **Manju Taxak**, S. Kumar, S. Sheelvantra, N. Krishnamurthy, Pressure-composition-temperature relationships in tantalum-iron-hydrogen solid solution, to be communicated.
10. **Manju Taxak**, N. Krishnamurthy, Hydrogen Absorption Kinetics of Tantalum-Aluminium Alloys, to be communicated.
11. **Manju Taxak**, S. Kumar, N. Krishnamurthy, Solubility of Hydrogen in Tantalum-Aluminum Alloys, to be communicated.

THANK YOU





Ta-Fe Phase Diagram [86 Swartz]