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Change in lattice parameter of tantalum due to dissolved hydrogen

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Abstract

The volume expansion of tantalum due to the dissolved hydrogen has been determined using Bragg equation. The hydrogen was dissolved in the pure tantalum metal at constant temperature (360 °C) and constant pressure (132 mbar) by varying the duration of hydrogen charging. The amount of dissolved hydrogen was within the solid solubility limit. The samples with different hydrogen concentration were analyzed by X-ray diffraction technique. Slight peak shifts as well as peak broadening were observed. The relative changes of lattice parameters plotted against the hydrogen concentration revealed that the lattice parameters varied linearly with the hydrogen concentration.

***Keywords**: tantalum, hydrogen, crystal structure, X-ray diffraction*

I. Introduction

A unique combination of physical and chemical properties makes tantalum a valuable material for high temperature and advanced technological applications. These properties are high melting point, good heat and electrical conductivity, high ductility and corrosion resistance. It has various applications in the medical field due to its good biocompatibility with the human body fluids. It is also used in the construction of high temperature furnace components and as hardware in high temperature environments such as heat shielding of jet engines and vacuum furnaces. Tantalum crucibles are used for high temperature processes, like fusion, thin film deposition, distillation and as heat exchangers. In the electronic industry, tantalum is used in manufacturing of capacitors, coils and boats for resistive evaporation. Tantalum is also considered as a promising candidate for the hydrogen separation membrane because of its superior mechanical strength compared to the palladium or ceramic based hydrogen separation membranes. The surface oxidation and hydrogen embrittlement are two key issues to be resolved before its selection for any specific application. Surface oxidation can be minimized by coating with thin palladium layer and hydrogen embrittlement can be reduced by alloying it with the materials like Ni and Mo [1–5]. Further, substitutional impurities can be used to modify the elastic interaction between the hydrogen and parent lattice.

In this context, it is essential to study the solid solution behaviour of tantalum-hydrogen system. The dissolved hydrogen induces distortions into the tantalum lattice and as a consequence leads to the changes in the volume of the crystals [1,5–7]. The dissolved hydrogen atoms are located on the tetrahedral interstitial sites. The local tetragonal symmetry of the defects sites is not transmitted to the long range displacement field, which shows cubic symmetry [6]. The elastic interaction of the dissolved hydrogen atoms with dislocations, impurities and other hydrogen atoms give rise to the overall dilation of the unit cell.

In the present investigation, varying amounts of hydrogen were introduced in the samples of tantalum metal. Lattice parameter was estimated quantitatively at different hydrogen concentrations using Bragg equation, and changes in the lattice parameter with respect to hydrogen concentration were determined.

II. Experimental

Several methods of hydrogen charging are given in the literature [8–10], but in the present investigation, hydrogen charging was carried out in a Sievert's appa-

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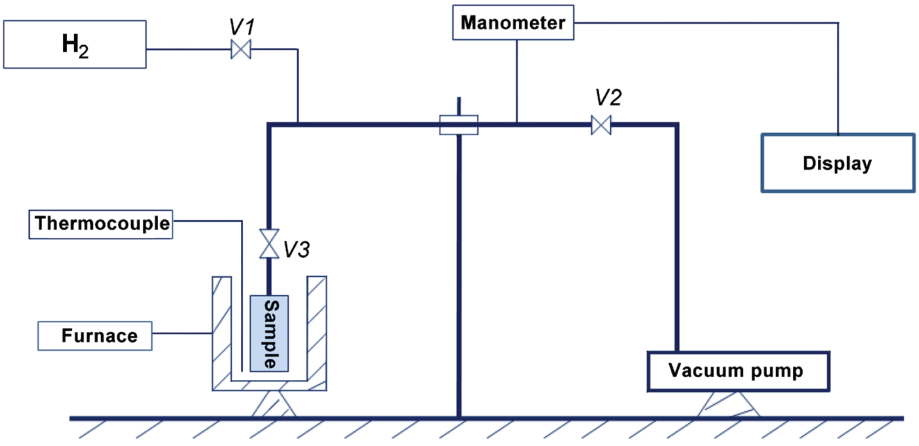

Figure 1. Schematic diagram of Seivert's apparatus

ratus using 99.999% pure hydrogen gas. A block diagram of the apparatus is shown in Fig. 1. The apparatus consists of a reaction chamber made of quartz, vacuum system, sample holder and a temperature controlled furnace. The furnace can be moved up and down manually in order to heat the reaction chamber whenever it was necessary. Along with furnace temperature, sample temperature was separately measured by placing a K-type thermocouple adjacent to the sample. Hydrogen gas can be introduced into the system in a controlled way. The capacitance manometer and display unit were used to read the pressure changes. For hydrogen charging, the tantalum foil (99.9% pure supplied by local vendor of Aldrich make) was cut into small samples of dimension 20 mm × 0.25 mm × 15 mm. These samples were mechanically polished and chemically cleaned using dilute acid mixture (45% HF + 45% HNO_3 + 10% H_2O). The freshly cleaned samples were immediately introduced into the argon gas filled hydrogen charging apparatus. The apparatus was evacuated up to 10^{-5} mbar and the sample was heated up to 900 °C for one hour to activate the sample surface and then cooled to the required temperature, 360 °C. The sample was isolated from the vacuum system and then hydrogen was introduced into the tube above the isolated sample holder up to the levels of hydrogen pressure 132 mbar, keeping the sample holder isolated from the hydrogen filled apparatus. The sample holder was then connected to the apparatus and the pressure was quickly adjusted to the predetermined level of 132 mbar. The hydrogen filling process was quite short, and hence, the influence of hydrogen absorption during filling process could be neglected. Upon the exposure of the samples to hydrogen, the hydrogen charging was initiated and a corresponding drop in the hydrogen pressure was observed due to the absorption of hydrogen by the sample. The instantaneous pressure drop was recorded with respect to time. The samples hydrogenated at identical conditions of hydrogen pressure and temperature for varying amounts of time were obtained in this manner. The dissolved hydrogen concentration was kept within the solubility limit by controlling the duration of hydrogen charging. The samples with different hydrogen concentrations were analyzed by X-ray diffraction (XRD) (Philips PW 1830) with Cr-Kα radiation at 30 mA and 40 kV using a curved position-sensitive detector, thus the diffraction data in complete 2θ range was observed.

III. Results and discussion

As indicated in the phase diagram [11], the terminal solid solubility of hydrogen in tantalum is around 800 ppm at room temperature. In the present investigation, the maximum concentration of hydrogen in the sample is 470 ppm as analyzed by inert gas fusion technique as well as by pressure drop method. The data shows that the concentrations of hydrogen present in the alloys are within the solid solubility limit. It is further verified by XRD analysis as no hydride phase is observed in the X-ray diffraction pattern as shown in Fig. 2. Based on the analysis of the XRD data, the distance between the two planes (d) is calculated using Bragg equation $n\lambda = 2d\sin\theta$ for three different θ values. Using these d values, the lattices parameter a is calculated by the following relation:

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

and, finally, the average value of lattice parameter a is determined. The values of lattice parameter a obtained for different hydrogen concentrations are shown in Fig. 3. The lattice parameter increases linearly with the increase of hydrogen concentration, obeying the Vegard's law [12]. The relative change in lattice parameter is shown in Fig. 4 and it is observed that the relative change in lattice parameter also depends linearly upon the hydrogen concentration as well.

The neutron diffraction study shows that hydrogen goes into interstitial sites in the metal lattice [13]. This causes an increase in the volume of the nearest-neighbour shell of atoms because the hydrogen atoms force

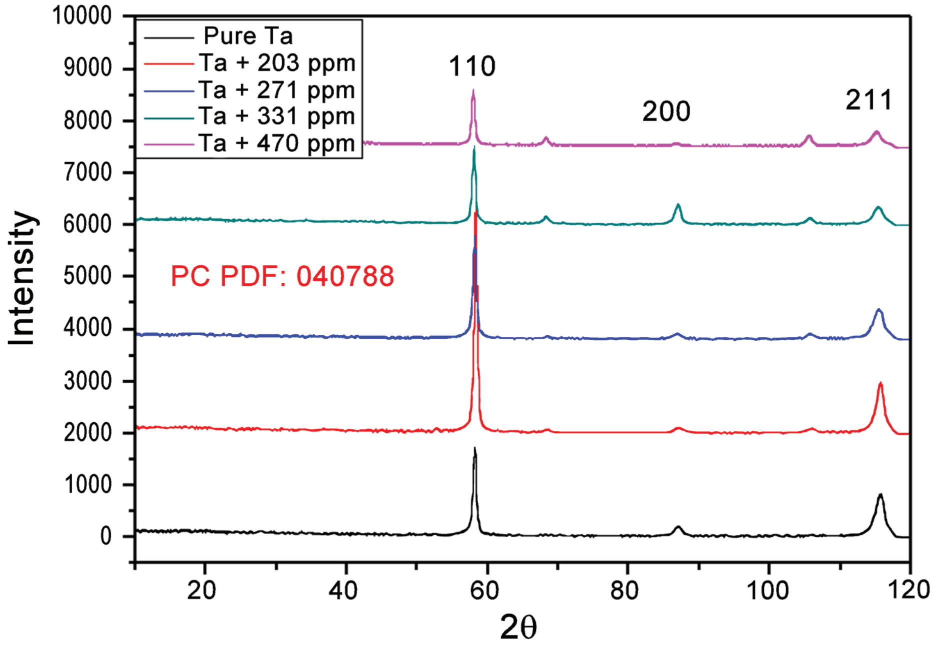

Figure 2. XRD analysis of pure and hydrogen charged sample

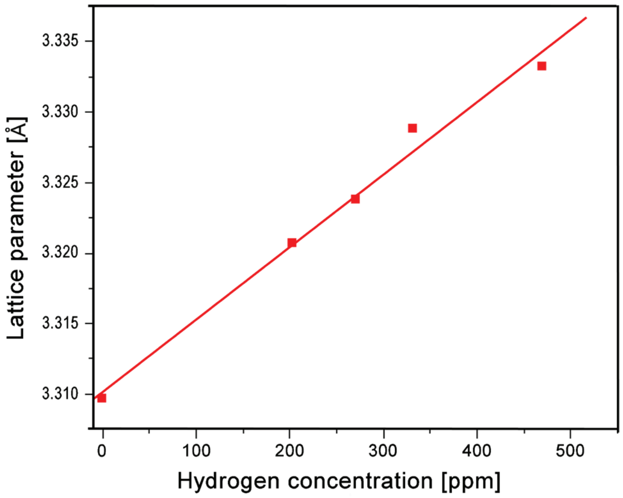

Figure 3. Lattice parameters of pure and hydrogen charged tantalum

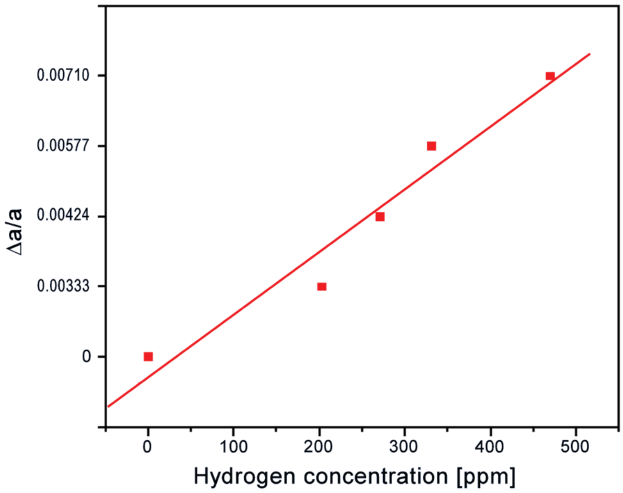

Figure 4. Relative changes in lattice parameters of hydrogen charged tantalum metals

the nearest-neighbour metal atoms to move away from each other. The free surface of the metal sample sweeps out to produce a larger volume increase than the volume increase of the inner shell of nearest-neighbour atoms. This is a physical phenomenon for the increase of the lattice parameter of the metal upon hydrogen absorption. At equilibrium, uniformly distributed dissolved hydrogen in a metal causes zero hydrostatic stress in the lattice, although each hydrogen atom is individually under a hydrostatic stress. There is no energy or pressure tending to push the hydrogen atoms together into one interstitial site.

The above observation could be explained by the density functional theory (DFT) [1,14–16]. The theory explained that irrespectively of other consideration, the electron density plays an important role in determining the lattice parameter. With the introduction of hydrogen into the metal matrix, the electron density in the valance band increases. As a consequence of increased electrostatic repulsion between electrons, the lattice parameter increases. The results obtained here follow the Vegard's law according to which, in solid solutions, lattice parameter is linearly varying with the concentration of solute. Many systems do not follow the Vegard's law because of other limitations, but in the present case the results seem to obey the Vegard's law.

IV. Conclusions

The lattice constant as well as the relative change in lattice parameters of the tantalum-hydrogen alloys increases linearly with the increased hydrogen concentration up to the solid solubility limit, obeying the Vegard's law. Measuring the change in lattice parameter due to the hydrogen ingress can be used to determine the concentration of hydrogen in the solid solubility range. Furthermore, the experimental data are in accord with the prediction of DFT theory.

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