Kinetic and structural aspects of tantalum hydride formation

B. R. SIMONOVIĆ[1,*], S. V. MENTUS[2] and R. DIMITRIJEVIĆ[3]

[1]*Holding Institute of General and Physical Chemistry, Studentski trg 12, 11000 Belgrade,* [2]*Faculty of Physical Chemistry, University of Belgrade, Studentski trg 12, 11000 Belgrade and* [3]*Faculty of Mining and Geology, University of Belgrade, Djušina 7, 11000 Belgrade, Serbia and Montenegro*

Abstract: Tantalum hydrides of various composition were synthesized by equilibrating tantalum with hydrogen at six different temperatures from 573 to 823 K, under a constant hydrogen pressure of 1 bar. Both the exact Ta/H mole ratios and the kinetic parameters of hydriding were determined on the basis of the dependence of the H/Ta mole ratio on time. The influence of stoichiometry on the appearance of X-ray powder diffractograms at room temperature was studied. As a consequence of hydriding, for ratios H/Ta > 0.2, the original bcc Ta-lattice undergoes distortion, manifesting itself as both a shift and a splitting of the X-ray patterns in the X-ray diffractograms. For samples with H/Ta < 0.2, the appearance of some superstructure reflections at low Bragg angles was noted, which suggests a long range ordering of hydrogen with orthorhombic symmetry.

Keywords: tantalum, hydriding isotherm, hydriding capacity, X-ray diffractometry.

INTRODUCTION

According to the phase diagram of the Ta–H system, published by Ducastelle *et al.*[1] and later revised by Schober and Carl,[2] nine ordered phases of tantalum hydride of different stoichiometries have been shown to exist at low temperatures, but only the disordered α-phase exists at temperatures higher than 350 K. A review concerning the order–disorder transitions in group V transition metals hydrides (V, Ni and Ta hydrides) was published by Hyrabayashi and Asano.[3] The methods used for the structural investigations in these works were neutron diffraction and thermal analysis.[1–3] The order–disorder transition in metal hydrides is linked to the presence of interstitial atoms in the host metal lattice. Interstitial hydrogen atoms are located in either tetrahedral (T–) or octahedral (O–) interstitial positions. The number of T– and O– sites per unit cell, available for hydrogen atoms (usually 12 and 6, respectively), is much larger than the number of hydrogen atoms per unit cell (usually less than 2). Therefore, ordered hydrides are easily transformed to disordered phases on heating. Such a transition may be detected as a pronounced jump in the thermal capacity.[3] Depending of the M/H mole ratio, a variety of ordered hydride phases along the composition axis of the phase diagram may exist, for instance M_2H, M_3H_2, M_4H_3, MH, *etc*.

---

*   Coresponding author.

Metal–hydrogen systems have been treated as quasimonocomponent systems composed of hydrogen atoms dissolved in the host metal lattice.[4] According to this opinion, the displacement of hydrogen atoms through the lattice corresponds to a polymorphic transition.

The host metal lattice distorts itself locally around the hydrogen atoms.[3] The distortion linked to an elastic displacement of the metal atoms causes a drop in the free energy. The transition temperature of a hydride depends on the latice parameters, *i.e.*, it decreases with increasing unit cell dimensions, as already postulated in the theory of elasticity.[3]

The available literature lacks in data on the kinetics of tantalum hydriding and on X-ray diffractometry of Ta–hydrides. Pick,[5] for instance, published some general considerations on hydrogen absorption. In our previous work,[6] investigations on the kinetics of tantalum hydriding were commenced. In the present paper, the hydriding kinetics in the temperature region in which only one phase, disordered α-TaH$_x$, exists (x is the number of H-atoms pro one tantalum atom) are discussed in more detail. The room-temperature X-ray diffractograms of samples of various stoichiometries were recorded, and the composition induced particularities are discussed.

EXPERIMENTAL

Hydriding experiments were carried out using high purity tantalum powder (+99.98 %, quality for tantalum solid electrolytic capacitors production) with an average grain size of 9 μm.

A typical volumeric apparatus consisting of a quartz tube containing a weighed quantity of tantalum powder was thermostated at a given temperature using a tube furnace. The compartment containing the tantalum powder sample could be connected either to a vacuum or to a hydrogen reservoir using a set of valves. Each sample was pretreated just before hydriding, *i.e.*, a complete annealing at 823 K, under a vacuum of 5×10^{-3} mm Hg during 2 h was undertaken. The stability of the vacuum during 15 min at 873 K, measured using a differential manometer, was used as a measure of the completeness of annealing. A constant pressure was an evidence that volatile componenets are no langer present in the sample.

At a hydrogen pressure close to the atmospheric one, the tantalum powder samples were subjected to hydriding at a constant temperature in the temperature range 573 – 823 K. According to the literature data,[2,3] only the α-phase of tantalum hydride exists in this temperature range. After each hydriding procedure, complete dehydriding was undertaken under experimental conditions identical to those under which the pretreatment was done.

The hydriding reactions always started at a hydrogen pressure equal to the atmospheric one and the quantity of hydrogen absorbed was determined as a function of time by measuring the pressure decrease. The relative pressure drop never exceeded 5 % and, therefore, one can treat the experimental conditions as being isobaric.

The absorption isotherms were determined at six different temperatures (573, 623, 673, 723, 773 and 823 K). Some of samples were palladized, by wetting with 0.03 % w.w. water solution of PdCl$_2$ and drying at 473 K.

For the X-ray diffractommetry (XRD) experiments, the samples hydrided at a certain temperature up to saturation were separated from the hydrogen reservoir by closing the connecting valve in order to avoid further hydrogen absorption during the cooling procedure. The diffractograms were recorded *ex situ* after cooling the hydrided samples to room temperature.

The XRD patterns were recorded by means of Philips PW-1710 automated diffractomeer using a Cu-tube operated at 40 kV and 30 mA. The instrument was equipped with a diffracted beam curved graphite monochromator and Xe-filled proportional counter. The diffraction data were collected in the 2θ range from 4º to 90º counting for 0.25 and 2.5 s in 0.02 steps. A fixed 1º divergence slit and 0.1º receiving slit were used. Silicon powder was used as a standard calibration of the diffractometer. All XRD patterns were recorded at room temperature.

RESULTS AND DISCUSSION

The time dependent volume of hydrogen absorbed by a weighed tantalum sample was used to calculate the hydrogen to tantalum mole ratio (H/Ta) as a function of time. This value as a function of time for all the studied temperatures is shown in Fig. 1. Obviously, the hydriding proceeds very slowly below 573 K. For instance, the volume of hydrogen absorbed at 523 K was negligibly low even after 24 h. The hydriding proceeds at a reasonable rate at a temperature of 573 K or higher. Therefore, the time needed to achieve maximal hydriding capacity is temperature dependent. At a temperature of 573 K this time is 50 h, and at 823 K, it amounts to only 10 min. However, as the temperature increases so the hydriding capacity decreases. The temperature of 873 K, at which the absorption capacity amounts to only 0.04, appears to be the limiting temperature at which hydriding is observable at all.

The temperature dependent hydriding capacities, expressed as the maximum H/Ta mole ratio, as determined from the long time parts of the absorption isotherms, are 0.55, 0.46, 0.39, 0.30, 0.22 and 0.13 for the temperatures 573, 623, 673, 723, 773 and 823 K, respectively. The H/Ta mole ratio decreases with increasing temperature which means that the equilibrium of the hydriding reaction $Ta + x/2\ H_2 = TaH_x$ is shifted towards the left. Therefore, the composition of the formed hydrides depends on temperature. If the composition is expressed by the formula TaH_x, x as a function of temperature varies from 0.55 to 0.13 in the temperature range 573 – 823 K.

The activating role of palladium in hydriding reactions is well known.[7] Palladium, dispersed on a metal or oxide surface, is capable of adsorbing molecular hydrogen. The adsorbed hydrogen molecules dissociate to hydrogen atoms adsorbed on the metal surface. The adsorbed atoms are able to diffuse along the surface as well as to spill over into the bulk of supporting material. As a result, palladium atoms accelerate the penetration of hydrogen atoms across surface boundaries. It may be noted that a small quantity of palladium (0.03 % w.w.) added to tantalum by thermal decomposition of $PdCl_2$, accelerates significantly the rate of hydriding. By comparing the initial slopes of the hydriding isotherms of both pure and palladized tantalum, it can be calculated that the hydriding rate at 673 K is about 30 times higher for palladized than for the pure sample. As a microcomponent, palladium does not affect the hydriding capacity, but significantly reduces the time required to achieve the maximum hydrogen content. The palladization procedure was used to accelerate hydriding in the temperature range 573 – 673 K for the purposes of the present study.

The significant influence of the presence of the catalyst on the tantalum surface on the hydriding kinetics helps the question concerning the nature of the slow step of hydriding to be answered. Namely, it can be assumed that the slow step is either the dissociation of adsorbed hydrogen molecules onto the surface of the tantalum particles, or the diffusion of hydrogen atoms through the tantalum bulk. Since, under isothermal conditions, the presence of traces of palladium accelerates the hydriding by a whole order of magnitude, it is obviously that the surface process, *i.e.*, the dissociation of hydrogen molecules to atoms, is the slow step. The heat of adsorption of molecular hydrogen onto tantalum is obviously

lower than the heat of dissociation to adsorbed atoms. Contrary to this, on a palladium surface, these heat values are better balanced and, therefore, the dissociation is much more pronounced, which explains the high hydriding rate of palladized tantalum.

On the basis of the here preassumed concept, the slow step of the hydriding is the reaction:

$$1/2 \ H_2 + S = H–S$$

where S is a site available for dissociation. The concentration of these sites is, however, time dependent, and decreases with the advance of the hydriding:

$$S = k_1(a - x) \tag{1}$$

where a is the initial Ta mole fraction, and x is the mole fraction transformed to hydride.

Therefore, the rate of hydriding may be exprsed by the following equation:

$$\frac{dx}{dt} = kp_{H_2}^{1/2}(a - x) \tag{2}$$

where the rate constant k involves also the constant k_1.

Since the hydriding was studied under practically isobaric conditions, *i.e.*, $p_{H_2} = const.$, this kinetic equation for the case under consideration may be presented in the following integrated form:

$$\log k = \frac{2.303}{t} \log \frac{a}{a - x} \tag{3}$$

The isotherms in Fig. 1 obey this equation very well, *i.e.*, the dependence log ($a/(a–x)$) *versus* time is linear, as shown in Fig. 2. The fact that the unique Eq. (3) may be used for all hydride compositions is most probably due to the unique crystallografic form (α-Ta–hydride) charcteristic for all compositions at a temperature above 323 K. From the slopes of the lines in Fig. 2, the rate constants were determined for each temperature, and their Arhenius plot enabled the energy of activation of tantalum hydriding to be calculated as 56.2 kJ/mol.

Figure 3 shows typical XRD patterns of the initial Ta–metal and its hydrides of various composition, recorded after cooling the samples to room temperature. Here is important to emphasize that, when cooled from the synthesis temperature to ambient temperature, some of the hydrides may be transformed to ordered phases. It is known from neutron diffraction measurements that at temperatures above 323 K the hydrogen atoms are randomly distributed through the tetrahedral and octahedral interstitial sites[1–3,8] of the BCC metal lattice, forming disordered α-Ta–hydrides. At temperatures unde 298 K, Ta–hydrides rich enough in hydrogen (*i.e.*, H/Ta > 0.2), may, at least partly, become ordered with a preferential occupation of hydrogen in specific sites, *i.e.*, Ta–hydrogen ordered phases, called β-Ta–hydrides, appear. The metal lattices of such prepared Ta–hydrides will be slightly distorted from the original cubic symmetry due to the non-cubic configuration of the trapped hydrogen atoms. Since hydrogen atoms are non-reflective
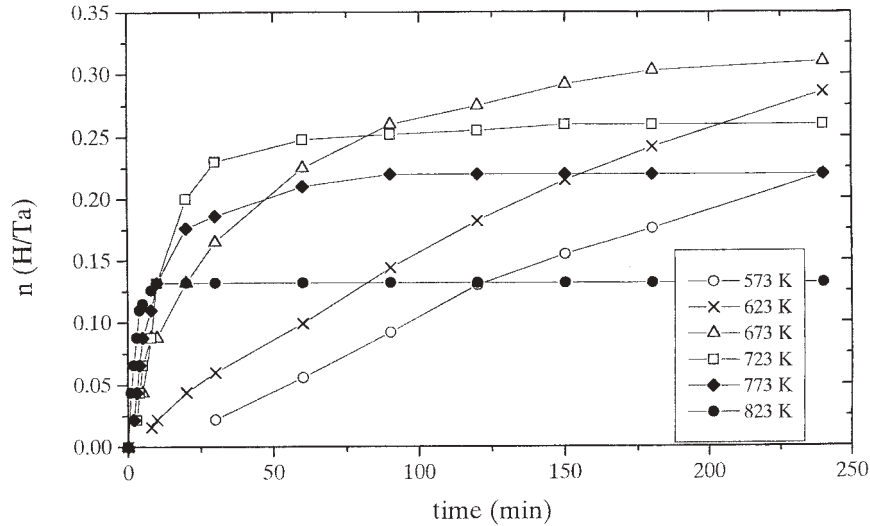
Fig. 1. The initial parts of the hydrogen absorption isotherms of tantalum at various temperatures.
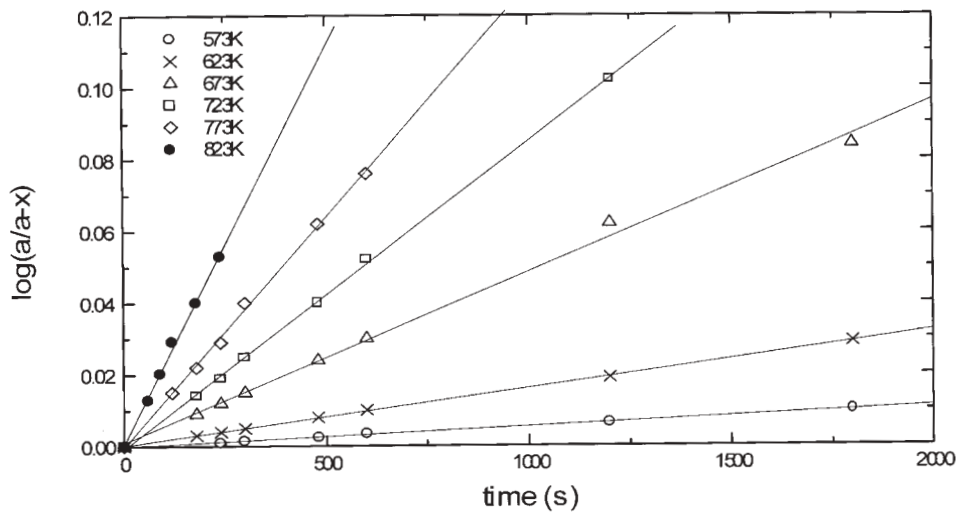

Fig. 2. log $(a/(a–x))$ vs. time plot for tantalum hydriding at different temperatures (a is the starting mole fraction of Ta, and x is the mole fraction of Ta–hydride formed in time t.

for X-rays, the crystallographic planes occupied by H atoms cannot be detected by XRD. Hovever, as can be seen in Fig. 3, where the XRD patterns of Ta–hydrides of various stoichiometry are presented, the distortion of the tantalum crystal latice is clearly visible. It is obvious from this Figure that the maximal distortion of the initial Ta-lattice (curve a) occurs in hydrides formed between 573 and 723 K, when $TaH_{0.55}$, $TaH_{0.46}$, $TaH_{0.39}$ and $TaH_{0.30}$ are formed (curves b–e), which according to the phase diagram (1) belong to or-dered phases. The ordered characteristics of the discussed hydrides manifest themselves by a systematic shift and splitting of the X-ray pattern in relation to the ones of pure tan-
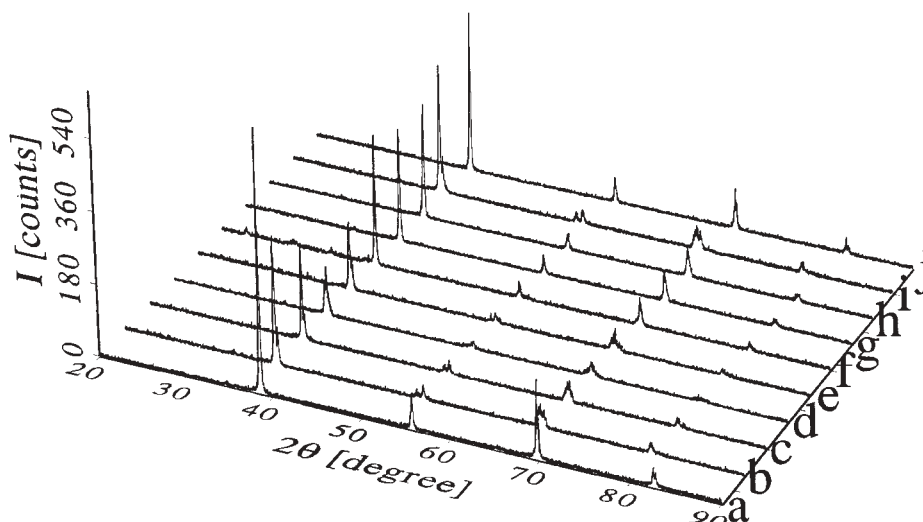
Fig. 3. Room temperature XRD paterns of the original Ta–metal powder (curve a), Ta–hydride powder synthesized at different temperatures (b – 573 K, c – 623 K, d – 672 K, e – 723 K, f – 773 K, g – 773 K, h – 833 K). The Ta–hydride with maximal hydrogen content after 5 hydriding/dehydriding cycles at 573 K, (curve i), and pure Ta–metal which was dehydrided completely after 5 cycles of hydriding/dehydriding (curve j).

talum. These patterns may be indexed in the orthorhombic symmetry as $A = 2\sqrt{2a}$, $B = \sqrt{2a}$ and $C = 2a$, where a is the Ta–metal BCC lattice parameter. However, it is obvious that the nature of the ordering is changed for Ta–hydrides with low hydrogen content, *i.e.*, those prepared above 773 K, Fig. 3 (curves f–h). Namely, according to the phase diagram (1), these hydrides remain in the disordered alpha form at room temperature. Accordingly, the X-ray powder patterns of $TaH_{0.22}$, (773 K, the first hydriding) (f) $TaH_{0.20}$ (773 K, the second hydriding, (g) and $TaH_{0.13}$ (823 K) (h), do not show peak splitting. The fundamental characteristic of these patterns is the appearance of superstructure reflections at low Bragg angles, suggesting a long range hydrogen ordering, *i.e.*, long range modulation of the host Ta–metal lattice. Therefore, the obtained powder patterns could be indexed on multiplied host Ta–lattice only.

Apart of the influence of temperature, the XRD results show that the appearance of a Ta crystall lattice depends also on the number of hydriding/dehydriding cycles. This was tested by hydriding a sample several times at 573 K, Fig. 3 (curve i), at which temperature hydrogen-rich hydrides are formed. The registered pattern shows prominent modulations corresponding to the mentioned orthorhombic symmetry. The same results were registered again with samples doped with traces of Pd. Finally, in order to check whether the hydriding/dehydriding processes induce permanent changes in the Ta-host lattice, the powder pattern of the multiple hydrided sample was taken after its complete dehydriding (Fig. 3, curve j). This pattern does not show any variation from the Ta-host BCC cubic lattice given by curve a. However, a somewhat reduced line intensity is noted, indicationg a crushing, *i.e.*, partial amorphisation, of the Ta particles during the hydriding/dehydriding cycles.

ИЗВОД

КИНЕТИЧКИ И СТРУКТУРНИ АПСЕКТ ФОРМИРАЊА ТАНТАЛ ХИДРИДА

Б. Р. СИМОНОВИЋ[1], С. В. МЕНТУС[2] и Р. ДИМИТРИЈЕВИЋ[3]

[1]*Холдинг инсиtиtуt за оpшtу и физичку хемију, Сtуденtски tрg 12, 11000 Беоgрад*, [2]*Факулtеt за физичку хемију, Универзиtеt у Беоgраду, Сtуденtски tрg 12, 11000 Беоgрад и* [3]*Рударско-gеолошки факулtеt, Универзиtеt у Беоgраду, Ђушина 7, 11000 Беоgрад*

Хидриди тантала различитог састава синтетисани су уравнотежавањем праха тантала са водоником на 6 различитих температура између 573 и 823 K, при константном притиску водоника од 1 бар. На основу зависности молског односа Ta/H од времена одређен је максималан садржај водоника као и константа брзине хидрирања за сваку од посматраних температура. Разматран је и утицај састава хидрида на изглед дифрактограма X-зракова на собној температури. Као последица хидрирања, за однос H/Ta > 0.2, оригинална bcc Ta-решетка трпи дисторзију што се огледа у померању и цепању линија дифрактограма. За хидриде код којих је однос H/Ta < 0.2, који према литератури на собној температури постоје само као неуређена фаза α-TaH$_x$, констатоване су суперструктурне рефлексије при малим Bragg-овим угловима, што указује на уређеност водоника дугог ранга са орторомбичном симетријом.

(Примљено 25. марта 2003)

REFERENCES

1. F. Ducastelle, R. Caudron, P. Costa, *J. Phys. Chem. Solids* **31** (1970) 1247
2. T. Schober, A. Carl, *Scripta Metallurgica* **11** (1977) 397
3. M. Harabayashi, H. Asano, "Order-disorder phenomena in metal hydrides" in *Metal Hydrides*, G. Bambakidis, Ed., Plenum Press, New York, 1981, pp. 53–80
4. G. Alefeld, *Phys. Stat. Sol.* **32** (1969) 67
5. M. A. Pick, "The kinetics of hydrogen absorption", in *Metal Hydrides*, G. Bambakidis, Ed., Plenum Press, New York, 1981 pp 329–343
6. B. R. Simonović, S. Mentus, M. V. Susic, *Int. J. Hydr. Energy* **25** (2000) 1069
7. W. C. Conner, J. L. Falconer, *Chem. Rev.* **95** (1995) 759
8. V. A. Somenkov, S. Sh. Shilstein, *Z. Phys. Chem. N. F.* **117** (1979) 125.