ELSEVIER

Journal of Alloys and Compounds 227 (1995) 167–174

Journal of
ALLOYS
AND COMPOUNDS

On the necessary experimental conditions to grow titanium films on hot tungsten filaments using titanium tetraiodide

F. Cuevas, J.F. Fernández, M. Alguerö, C. Sánchez*

Dpto. Física de Materiales C-IV, Universidad Autónoma de Madrid, Cantoblanco 28049, Madrid, Spain

Received 5 December 1994; in final form 20 March 1995

Abstract

An experimental system has been built to grow titanium films on hot tungsten filaments by the pyrolytic decomposition of titanium tetraiodide. Different procedures are examined in this system to establish the necessary experimental conditions to promote titanium deposition. The experimental results are analyzed considering the thermodynamics of the deposition reaction. It has been found that the iodine partial pressure around the hot filament is the more relevant parameter to dictate the deposition feasibility and must always be kept lower than 10^{-2} atm for typical TiI_4 partial pressures. This statement applies to the dynamic experiments performed in our laboratory using titanium tetraiodide and also to the cyclic experiments performed by other authors using crude titanium and iodine. The morphology of the deposited films is also discussed.

Keywords: Titanium; Titanium tetraiodide; Thermal decomposition; Vapour deposition; Film growth

1. Introduction

It is well known that titanium and titanium alloys are excellent systems for hydrogen (deuterium) absorption and storage [1,2]. Besides, recent investigations have arisen in relation to the occurrence of anomalous nuclear effects in titanium deuterides [3]. These phenomena seem to be deeply influenced by some host metal characteristics such as purity, surface state and structural bulk properties. In this context, our laboratory is dealing with the production of titanium by means of the iodide process to obtain high-purity titanium of controlled crystallographic characteristics to be used in such investigations.

The production of titanium by the iodide process, also known as the hot-wire process, was developed by Van Arkel and De Boer in 1925 [4]. The purification method starts with the reaction between iodine and impure titanium in excess to release volatile titanium iodides near to room temperature. Then, iodide vapors decompose in the presence of a tungsten filament electrically heated at high temperatures. Consequently, titanium deposits on the filament while iodine reacts again with the impure titanium in a cyclic process.

Up to the middle of the current century the method was focused to try to produce ductile titanium on an industrial scale [5,6] for nuclear energy and aerospace applications. Unfortunately, some technical problems (mainly overheating of the operational system) which appear when large quantities of titanium are deposited put the method out of the industrial scope. Nevertheless, some scientists are still researching this process owing to the interest of the high-purity resulting material. Different aspects of this technique have been analyzed: the lower iodides' behavior, which can limit the titanium deposition [7,8], as pointed out previously by Fast [9], thermodynamics of the process [10,11], metal quality [12,13] and morphology [13,14].

In spite of such work, the relationship between the deposited metal characteristics and the process parameters remains unclear owing to the appearance and intricate behavior of the different iodides that are involved in the system [7,8,15–17]. Therefore, and in order to establish such a relationship, we have tested a simpler method based on using TiI_4 as the only starting material, avoiding the influence of the lower iodides.

In this paper we present different experimental

---

* Corresponding author.

0925-8388/95/$09.50 © 1995 Elsevier Science S.A. All rights reserved
SSDI 0925-8388(95)01644-9

procedures that were examined in our laboratory to deposit iodide titanium using TiI_4 as starting material. The feasibility of titanium deposition in these experiments is discussed and explained considering an accurate thermodynamic analysis of the process. The morphology of the deposited films is also discussed.

2. Experimental

The apparatus designed for the titanium deposition is shown in Fig. 1(A). As titanium tetraiodide is extremely hygroscopic and reactive, Pyrex glass was chosen as the construction material. The apparatus is composed of a central chamber (70 mm O.D.) which contains the initial tungsten filament (0.3 mm O.D., 7 cm length U-shaped) welded to two tungsten electrodes (1 mm O.D.). Two side arms, one for joining the TiI_4 bulb and the other for pumping connection and pressure measurement, complete the reactor.

1.9 g of 99% TiI_4 from Johnson Matthey were placed in a small bulb under argon atmosphere. This bulb was evacuated (10^{-3} Torr), sealed and attached to the left arm of the system. Afterwards, the whole system was placed into a transparent electric furnace and outgassed for 10 h at 525 K under mechanical pumping (10^{-3} Torr) through a liquid nitrogen (LN) trap. Meanwhile the tungsten filament was heated for 4 h at 1775 K by passing an alternating current through it and eventually the system was sealed. Next, the TiI_4 bulb was smashed by means of a magnetic striker and was slightly heated within the established operation range (350–525 K [7,9]) to attain a TiI_4 vapor pressure of 10^{-5}–10^{-2} atm [17,18]. Then, the filament was also heated within the range of temperatures where deposition is possible (1375–1825 K) [4]. Filament temperature was measured with an optical pyrometer, taking into account the spectral emissivities of tungsten [19] and titanium [20]. It is estimated that filament temperature measurements are accurate to about ± 15 K at low temperatures ($\approx$ 1400 K) and ± 30 K at high temperatures ($\approx$ 1800 K).

The quantity of deposited titanium was measured on-line in relation to the electric resistance variation of the filament at a given temperature. Considering the filament as two parallel resistances, the inner tungsten and the outer deposited titanium (neglecting interface phenomena), the deposited titanium quantity can be obtained from the following equation:

$$m_{\mathrm{Ti}} = d_{\mathrm{Ti}} L \frac{\rho_{\mathrm{W}}(T)\rho_{Ti}(T)L - R\rho_{Ti}(T)S_{\mathrm{W}}}{R\rho_{\mathrm{W}}(T)} \qquad (1)$$

where d_{Ti} stands for the titanium density, L is the filament length, S_{W} is the cross-sectional area of the initial tungsten filament, R is the resistance of the whole filament, and ρ_{Ti}(T) and ρ_{W}(T) stand for the electrical resistivity of titanium and tungsten, respectively, at the filament temperature.

After the end of the growth process, all filaments were analyzed by energy-dispersive X-ray analysis (EDAX), and scanning electron microscopy (SEM) micrographs were taken. A piece of each filament was embedded in plastic resin, polished with emery paper up to 7 μm, and slightly etched with FH:HNO_3:H_2O (1:2:22) to analyze its cross-section by the same techniques.

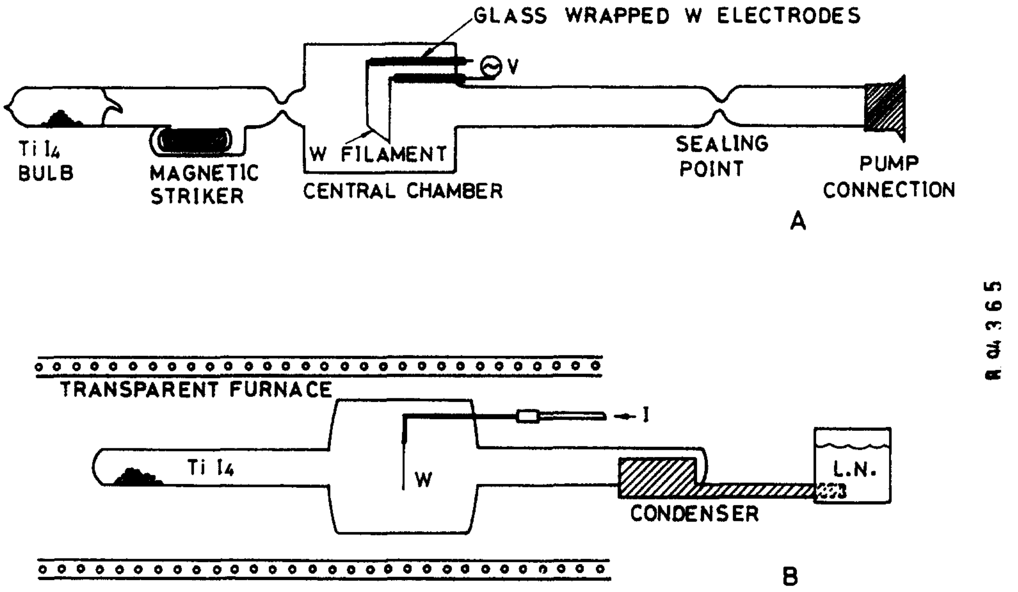


Fig. 1. (A) Pyrex glass reactor built to deposit iodide titanium films using TiI_4. (B) System configuration in unidirectional vapor flow experiments.

3. Results

Three different experimental procedures were carried out. The first one was able to maintain a steady TiI_4 vapor pressure in the reactor by keeping the whole system at constant temperature. The second experimental procedure was accomplished in a variable temperature gradient that forced TiI_4 vapors to pass over the tungsten filament several times. Finally, a unidirectional vapor flow experiment, i.e. a single step of the previous experiment, was carried out with the system configuration sketched in Fig. 1(B).

3.1. Steady vapor experiments

Several distinct values of TiI_4 and filament temperatures were tested within operational ranges of 350–520 K and 1375–1825 K, respectively. However, it was not possible to detect any mass deposition during the experiments from the measurement of electrical resistance variations of the filament. Besides, EDAX after the experiments did not detect any titanium deposition on the tungsten filament.

These results suggest that it is not possible to use a steady-vapor system to deposit an appreciable titanium mass. It was inferred that the TiI_4 decomposition reaction soon becomes stopped by the presence of the released iodine, according to a severe fulfillment of the Le Chatelier's principle. Therefore, some method must be implemented to evacuate iodine very efficiently from the filament area to get appreciable titanium deposition.

3.2. Reversible vapor flow experiments

A dynamic and reversible vapor-flow procedure was obtained with the help of an exchangeable cooling–heating system. TiI_4 was sublimated to the reaction chamber and the residual gases were condensed by cooling with LN at the opposite arm. Afterwards, when TiI_4 was completely sublimated, heating and cooling emplacements were exchanged to force condensed gases to pass again over the filament. Thus, several vapor circulations were done to try to deposit as much titanium as possible. Heater and condenser temperatures were 433 K and 175 K, respectively, whereas filament temperature was adjusted to 1575 K. A mass deposition was electrically detected during the process.

The resulting filament surface is uniform and flaky, displaying a spongy aspect, as can be observed in Fig. 2(A). However, when a more highly magnified SEM image was taken (Fig. 2(B)) two different morphologies could be clearly recognized: one has a porous layer structure while the other, being in a deeper level, has a polyhedral structure. The composition of the porous layer structures is mainly tungsten, as was recorded by a mapping EDAX (white dots in Fig. 2(C)); but small quantities of iodine were also detected in them. On the other hand, the composition of the polyhedral structures is only titanium. The cross-sectional micrograph of the filament (Fig. 2(D)) shows the tungsten substrate in the middle of the film, as a brighter disc (300 μm O.D.), surrounded by a titanium deposit (in a ray-shape structure) that is covered by tungsten–tungsten iodide films.

This experiment suggests that it is possible to deposit titanium using TiI_4 as starting material: however, no more than one vapor circulation should be done in this system to achieve a pure titanium film.

3.3. Unidirectional vapor flow experiments

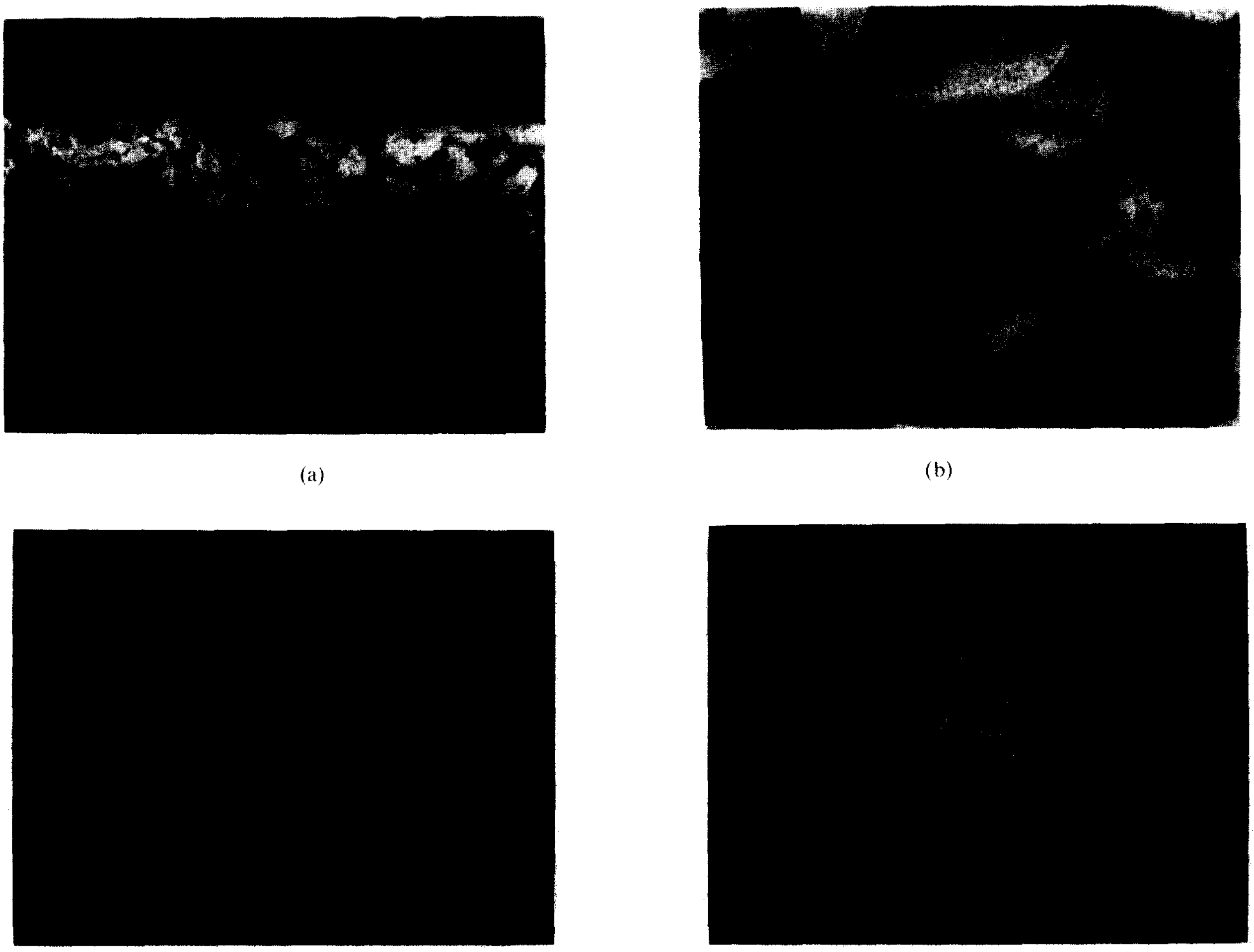
Finally, a unidirectional vapor flow experiment was carried out in order to try to deposit only titanium on the filament. The experiment was run at 413 K TiI_4 bulb and 1575 K filament temperatures. Continuous mass deposition was registered for 30 min. Then, deposition stopped because of the complete sublimation of the TiI_4 product.

The surface of the resulting filament and its cross-section were observed by SEM (Fig. 3(A) and Fig. 3(B)). The surface morphology is fairly smooth and homogeneous except for some rhombendodecahedral-shape structures (≈ 150 μm in size). EDAX measurements indicate that both morphologies are titanium, with neither tungsten nor iodine present at levels above the EDAX detection sensitivity (Fig. 4(A) and Fig. 4(B)).

The deposited titanium mass was weighed at 78 mg. The filament reached an average thickness of 650 μm, with tungsten and titanium phases clearly distinguishable, as shown in Fig. 3(B). The average rate of deposition, taking into account initial and final filament thicknesses, is calculated to be 151 mg cm^{-2} h^{-1}, i.e. an order of magnitude faster than the rate obtained in typical cyclic processes [7].

4. Discussion

It becomes clear that the achievement of titanium deposition using TiI_4 depends on an appropriate determination of the following experimental parameters: the TiI_4 bulb temperature that dictates the corresponding TiI_4 partial pressure, the filament temperature to establish the decomposition reaction temperature, and the accomplishment of a dynamic method to evacuate the residual by-product, iodine. A detailed thermodynamic analysis of the process will allow the giving of a theoretical background to the experimental results and the deduction of the com-



(a) (b)

(c) (d)

Fig. 2. Filament resulting from the reversible vapor flow experiment (3.2): (A) SEM image of the surface morphology; (B) SEM image of a magnified area of (A); (C) Tungsten location (white dots) in (B) detected by EDAX; (D) SEM image of the filament cross-section.

plete range of pressures and temperatures where titanium deposition can be obtained. In addition, the morphology of the resulting films is discussed later on.

In what follows, those experiments performed with titanium and iodine as starting materials will be denoted as "cyclic processes", while our flow experiments performed with TiI_4 (Sections 3.2 and 3.3) will be denoted as "dynamic processes".

4.1. Thermodynamics of the process and experimental deposition feasibility

The feasibility of titanium deposition in the different experiments can be analyzed considering the thermodynamics of the Ti–I system. At the low TiI_4 vapor pressures (10^{-2}–10^{-5} atm) and at the high temperatures (1300–1850 K) where deposition occurs, the reaction at the filament must be:

$$TiI_4(g) \rightarrow Ti(s) + 4I(g) \tag{2}$$

Gaseous iodine is completely dissociated [21] and lower iodides are expected to exist for a very short time on the filament at the temperatures and pressures mentioned [22].

The free-energy change (ΔG) in Eq. (2) can be properly calculated from the sum of three terms:

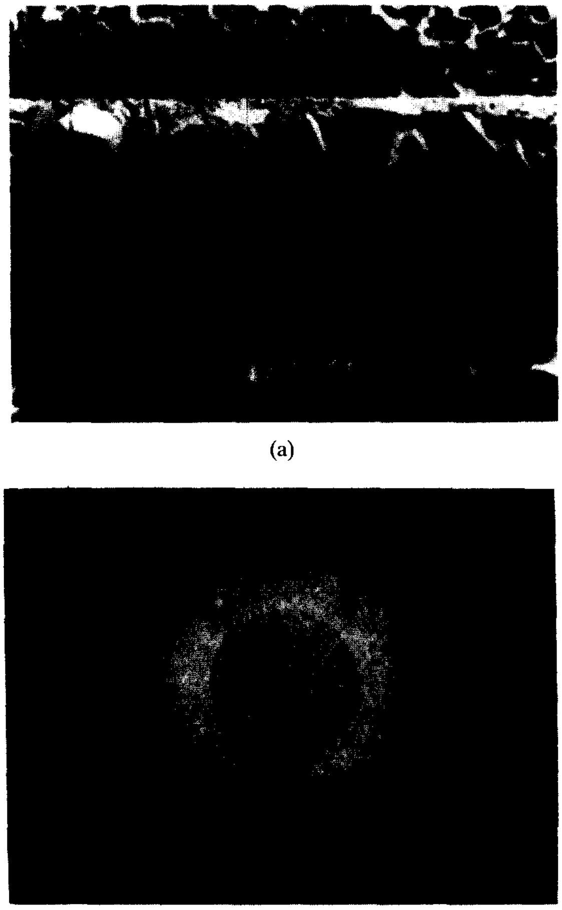
$$\Delta G = \Delta G_f^0 + \Delta G^0_{T-298.15} + \Delta G^p_T \tag{3}$$

where

$$\Delta G_f^0 = \left[\sum \Delta H_f^0(\text{prod.}) - \sum \Delta H_f^0(\text{reac.})\right] - T\left[\sum \Delta S_f^0(\text{prod.}) - \sum \Delta S_f^0(\text{reac.})\right] \tag{4}$$

$$\Delta G^0_{T-298.15} = \int_{298.15}^{T} \left[\sum \Delta C_p^0(\text{prod.}) - \sum \Delta C_p^0(\text{reac.})\right] dT - T \int_{298.15}^{T} \frac{\sum \Delta C_p^0(\text{prod.}) - \sum \Delta C_p^0(\text{reac.})}{T} dT + \Delta H^0_{\text{Ti}:\alpha\rightarrow\beta} - T\,\Delta S^0_{\text{Ti}:\alpha\rightarrow\beta} \tag{5}$$

$$\Delta G^p_T = RT \ln \frac{\Pi P(\text{prod.})}{\Pi P(\text{reac.})} \tag{6}$$



(a)

(b)

Fig. 3. Filament resulting from the unidirectional vapor flow experiment (3.3): (A) SEM image of the surface morphology; (B) SEM image of the filament cross-section.

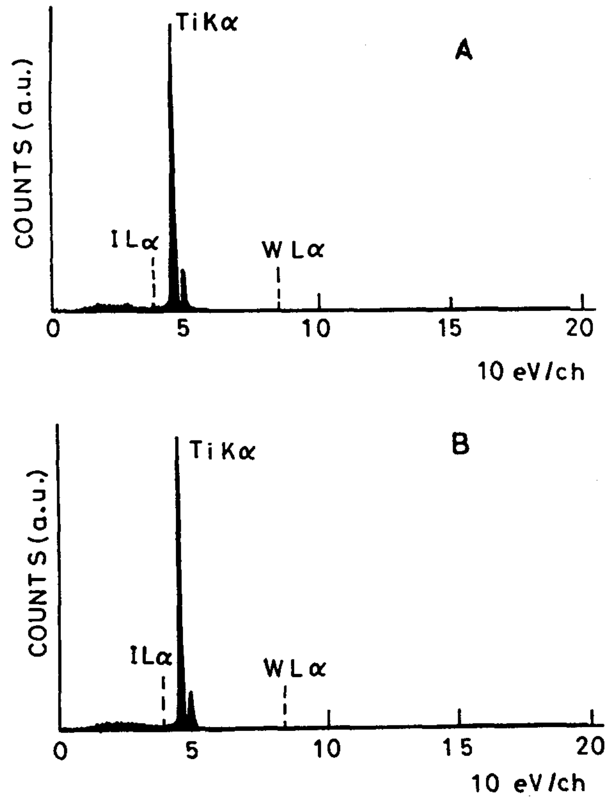


Fig. 4. EDAX analyses of (A) the uniform deposit and (B) large polyhedral structures in the unidirectional vapor flow experiment.

Eq. (4) stands for the standard free-energy change at room temperature of the reaction under study. The thermodynamic data used to get the standard heats and entropies of formation (ΔH_f^0 and ΔS_f^0, respectively) of the products (Ti(s) and I(g)) and reactants (TiI_4(g)) are given in Table 1. Selected values, particularly those corresponding to TiI_4, were chosen from the most reliable handbook tables and reported papers [21,23–26]. Eq. (5) is related to the variation of the standard free energy with the reaction temperature (T). To evaluate this equation, the data given in Table 2 for the standard heat capacities at constant pressure (C_p^0) of the compounds and the free-energy contribution due to the structural phase transition of Ti are used [21,27,28].

It should be remarked that the TiI_4(g) heat capacity vs. temperature relation was obtained by fitting and extrapolating the data obtained by Clark et al. [28] from the Raman spectrum of TiI_4(g) as shown in Fig. 5. Finally, Eq. (6) corresponds to the free-energy change considering the partial pressures of the gaseous species involved. Typical partial pressures of the gaseous products (P_I) and reactants (P_{TiI_4}) were considered, whereas the activity of solid titanium was taken as 1. Although a similar thermodynamic analysis was done by Shelton [10,29], the second term in Eq. (3) was not considered by him, and new thermodynamic data have appeared since then.

In conclusion, the free-energy change of the reaction is as follows

$$\Delta G = 169130 - 83.2T + 3.735\times10^{-3}T^2 - \frac{2.235\times10^5}{T} + 0.96T\ln T + 1.987T\ln\frac{P_I^4}{P_{TiI_4}}\ \text{cal mol}^{-1} \qquad (7)$$

This equation is depicted as an Elligham diagram in Fig. 6 for typical TiI_4 partial pressures of cyclic and dynamic processes (10^{-2} and 10^{-4} atm, respectively) at two representative iodine partial pressures (10^{-2} and 10^{-4} atm). Titanium deposition will occur as long as the free-energy change of the reaction is negative and its temperature is lower than the melting point of the metal.

Partial pressures of both gaseous species will dictate whether or not deposition is possible for a given reaction temperature. So it is clear from Fig. 6 that the influence of the iodine pressure on the deposition

Table 1
Standard heats of formation (ΔH_f^0) and standard entropies at room temperature ($S_{298.15}^0$) for the Ti–I species involved in the process

Compound	Ti(s)	I_2(s)	I_2(g)	I(g)	TiI_4(s)	TiI_4(g)
ΔH_f^0 kcal mol^{-1}	0	0	14.923	25.535	-92.2 ± 1.5^b	-68 ± 2^a
$S_{298.15}^0$	7.32	27.757	62.28	43.184	$60 \pm 2^{a,c}$	$103 \pm 1^{a,c,d}$

The data are from Ref. [23] except a, b, c, d taken from Refs. [21,24,25,26], respectively.

Table 2
Standard heat capacities at constant pressure for the species involved in the deposition reaction and transition Ti ($\alpha \rightarrow \beta$) enthalpy and entropy

Compound	C_p^0(T) (cal K^{-1} mol^{-1})		$\Delta H^0_{\text{transition}}$ (cal mol^{-1})	$\Delta S^0_{\text{transition}}$ (cal K^{-1} mol^{-1})
Ti(s)	$5.25 + 2.52 \times 10^{-3}$T	[298–1155 K]	950	0.822
[27]	7.50	[1155–2000 K]		
I(g)	$4.80 + 0.16 \times 10^{-3}$T $+ 0.11 \times 10^5$T^{-2}		–	–
[21]		[298–5000 K]		
TiI_4(g)	$25.74 + 0.07 \times 10^{-3}$T $- 1.05 \times 10^5$T^{-2}		–	–
[28][a]		[298–200 K]		

[a] C_p^0(T) of TiI_4(g) is calculated from the data reported by Clark et al. [28] and is extrapolated to 2000 K as shown in Fig. 5.

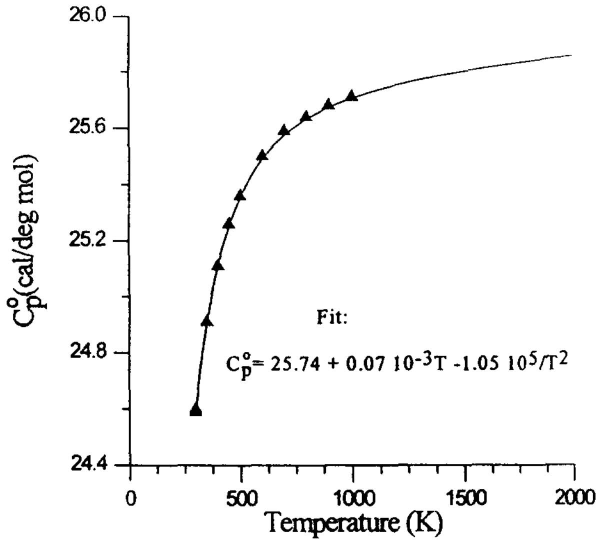


Fig. 5. Standard heat capacity vs. temperature of TiI_4(g). Data points (▲) are from Clark et al. [28]. Continuous line is the best fit to the data for a temperature power series: $C_p^0(T) = a + bT + cT^{-2}$. Fitting has been extrapolated to 2000 K.

feasibility is drastic. In fact, it can be concluded that deposition is actually not allowed when the iodine pressure is higher than about 10^{-2} atm. This statement explains why it was not possible to detect any mass deposition in our steady-vapor experiments (Section 3.1). Considering the system volume and temperature in the reaction chamber, this iodine pressure is attained when about 1 mg of titanium is deposited, and this quantity is not detected by electrical resistance variations of the filament. Consequently, iodine should be removed from the filament area to promote deposition, as done by the crude titanium in cyclic processes or by the cooling trap in our dynamic experiments.

An estimation of the capability of iodine depletion by these methods can be made. In cyclic processes ($P_{TiI_4} \sim 10^{-2}$ atm), deposition starts at a minimum temperature of 1375 K, so that the crude titanium is able to react with released iodine to decrease its pressure around the filament below 5×10^{-4} atm. Our dynamic experiments ($P_{TiI_4} \sim 10^{-4}$ atm, Sections 3.2 and 3.3) were carried out at a filament temperature of 1575 K, so that the cooling system was able to decrease iodine pressure around the filament at least to below 9×10^{-4} atm. Therefore, a similar gettering efficiency is observed to be produced in the evacuation of iodine by both methods.

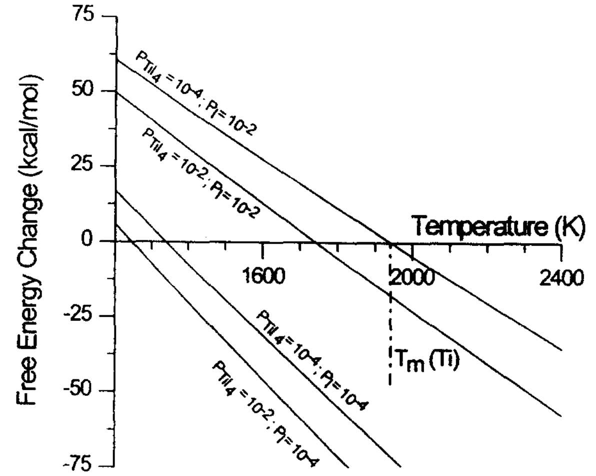


Fig. 6. Free-energy change vs. temperature curves for typical values of iodine and titanium tetraiodide partial pressures (in atm) obtained from Eq. (7). Melting point of titanium metal is also indicated as T_m(Ti).

A wider knowledge of the necessary experimental conditions to deposit titanium in both processes can be inferred from the iodine equilibrium pressure vs. filament temperature relationship. This relationship

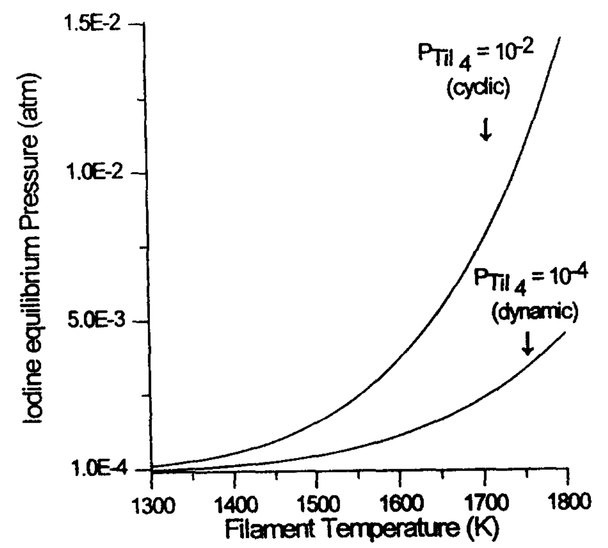


Fig. 7. Iodine equilibrium pressure vs. deposition temperature, obtained from Eq. (7) when $\Delta G = 0$, for two typical values of titanium tetraiodide partial pressure (in atm) corresponding to cyclic and dynamic growth processes.

(derived from Eq. (7), when $\Delta G = 0$) is plotted in Fig. 7 for typical TiI_4 partial pressures in cyclic and dynamic processes. In order to achieve continuous titanium deposition, the iodine partial pressure at the filament must always be kept lower than its equilibrium value at any given temperature (i.e. below the corresponding curve in Fig. 7). Hence, it seems that the temperatures and pressures accomplished in our TiI_4 flow experiments (Sections 3.2 and 3.3) were adequate to deposit titanium on the tungsten filament. Heating of the TiI_4 bulb to reach a constant temperature provides a constant TiI_4 pressure around the filament area, whereas the LN trap depletes the released iodine vapors very efficiently to reduce the pressure below its equilibrium value.

However, in the reversible experiment (Section 3.2), tungsten and tungsten iodide deposits grew on the previously deposited titanium film because of the several vapor circulations that were performed, as will be explained with more detail in the following section.

4.2. Morphology of the deposited films

The morphology and composition of the resulting filament in the reversible-vapor-flow experiment (Section 3.2) can be explained considering the attack of the tungsten electrode tips by the released iodine. During the first vapor circulation a thick titanium film was formed, while iodine and non-decomposed TiI_4 molecules were trapped in the condenser. In the following circulation the tungsten electrode tips were attacked by iodine vapors sublimated from the condensed material (this fact is supported by the well-known formation of tungsten iodide at about 1000 K from metallic tungsten and iodine [21]). Thus, tungsten iodide is formed in the electrode tips of the reaction chamber and later sublimated to the filament. Besides, some reported investigations [30] about the reaction between tungsten filaments and iodine indicate that at temperatures below 1445 K a film of tungsten iodide (about ten molecules in thickness) is formed on the filaments, being decomposed above 1505 K. Hence, the porosity and outer localization of tungsten–tungsten iodide deposits must be due to the formation and decomposition of the mentioned film after tungsten has been sublimated as tungsten iodide from the electrode tips.

In relation to the morphology of the pure titanium films obtained in the unidirectional experiment (Section 3.3) some considerations can be made concerning the appearance of the highly faceted crystals. These large deposits can be related to the presence of longitudinal fissures in the initial tungsten filaments according to the fibrous structure of commercial tungsten wires. The longitudinal location of these highly faceted crystals seems to support this idea. It is also worth remarking that these crystals reflect the cubic structure (fcc) presented by titanium metal at the temperatures where deposition takes place, as rhombendodecahedral structures develop from a habit growth on the {100} and {110} crystal planes of the cubic symmetry. Such planes have the highest atomic densities, so the faster deposition rates on them can be attributed to the tendency of titanium to form close-packed structures.

5. Conclusion

An experimental system has been developed to grow iodide titanium films on hot tungsten substrates, using TiI_4 as starting material. Pure titanium films can be achieved by means of a unidirectional TiI_4 vapor flow system as long as the filament temperature is lower than the melting point of the metal and the free-energy change of the reaction (Eq. (7)) is negative. Considering these conditions, it has been calculated that the iodine partial pressure around the filament must be lower than 10^{-2} atm for typical TiI_4 partial pressures. Static vapor experiments cannot operate, as the iodine partial pressure easily reaches this value and consequently the titanium deposition ceases. It has also been found that reversible-vapor-flow experiments are not adequate, as free iodine attacks the tungsten electrodes of the reaction chamber to deposit tungsten and tungsten iodide layers on the previously deposited titanium film.

Owing to the simplicity of the experimental system developed and the procedure followed to deposit pure titanium films, we believe that it will be possible to correlate the process parameters (filament temperature, iodide pressure, and substrate morphology) accurately with the characteristics of the deposited titanium (purity, crystallographic bulk structure and surface morphology).

Acknowledgments

The authors acknowledge financial support from Fundación Banco Exterior (Proyecto C-090/90) and CICYT (MAT-90-0053), and express their thanks to SEGAINVEX for their skillful glassblowing. The technical assistance of Mr. F. Moreno and Mr. A. Bergas is also recognized.

References

[1] G. Alefeld and L. Völkl, *Hydrogen in Metals, I. Application-Oriented Properties, Topics in Applied Physics, Vol. 29*, Springer, Berlin, 1978.
[2] W. Muller, J. Blackedge and G. Libowitz, *Metal Hydrides*, Academic Press, New York, 1968.
[3] S.E. Jones, F. Scaramuzzi and D.H. Worledge (eds.), in *Anomalous Nuclear Effects in D/Solid Systems, Conf. Proc., Vol. 228*, AIP, New York, 1991.
[4] A.E. van Arkel and J.H. de Boer, *Z. anorg. allg. Chem., 148* (1925) 345.
[5] I.E. Campbell, R.I. Jafee, J.M. Blocher Jr., J. Gurland and B.W. Gonser, *Trans. Electrochem. Soc., 93* (1948) 271.
[6] B.W. Gonser, *Metall Prog., 55* (1949) 193.
[7] O.J.C. Runnals and L.M. Pidgeon, *Trans. Amer. Inst. Min. (Metall.) Engrs., 194* (1952) 843.
[8] V.D. Shah, B.P. Sharma and C.M. Paul, *J. Less-Common Metals, 53* (1977) 109.
[9] J.D. Fast, *Z. anorg. Chem., 241* (1939) 42.
[10] R.A.J. Shelton, *Trans. Inst. Min. Met. (c), 77* (1968) 32.
[11] G.H. Kesler, *Trans. AIME, 218* (1960) 197.
[12] R.A.J. Shelton, *Trans. Inst. Min. Met. (c), 78* (1969) 111.
[13] F.B. Litton and B.W. Gonser, *Metall Prog., 55* (1949) 346.
[14] W.G. Burgers, *Physica, 1* (1934) 562.
[15] J.D. Fast, *Rec. Trav. Chim. Pays-Bas, 58* (1939) 174.
[16] B.G. Newland and R.A.J. Shelton, *J. Less-Common Met., 20* (1970) 245.
[17] R.A.J. Shelton, preprint, *Int. Conf. Adv. Chem. Metall.*, 2 Paper 46, 1979, p. 1.
[18] J.M. Blocher and I.E. Campbell, *J. Am. Chem. Soc., 69* (1947) 2100.
[19] Y.S. Toulokian, *Thermophysical Properties of High Temperature Solid Materials, Vol. 1*, Macquillan Company, Purdue University, 1967, p. 1019.
[20] F.J. Bradshaw, *Proc. Phys. Soc., 63* (1950) 573.
[21] R.F. Rolsten, *Iodide Metals and Metal Iodides*, Wiley, New York, 1961.
[22] A.C. Loonam, *J. Electrochem. Soc., 106* (1959) 238.
[23] C.T. Lynch, *Handbook of Material Science, Vol. 1*, CRC Press, 1974, pp. 292, 325.
[24] W.H. Johnson, A.A. Gilliland and E.J. Prosen, *J. Res. Nat. Bureau Standards A, 63A(2)* (1959) 161.
[25] A.F. Trotman-Dickenson, *Comprehensive Inorganic Chemistry*, Pergamon Press, 1973, p. 370.
[26] R.J.H. Clark and C.J. Willis, *J. Chem. Soc. A* (1971) 838.
[27] R.C. Weast, *Handbook of Chemistry and Physics*, CRC Press, Cleveland, OH, 55th edn., 1974, p. D-55.
[28] R.J.H. Clark, B.K. Hunter and D.M. Rippon, *Inorg. Chem., 11(1)* (1972) 56.
[29] R.A.J. Shelton, *Ph.D. Thesis*, Manchester, UK, 1962.
[30] G. Van Praagh and E.K. Rideal, *Proc. R. Soc. Lond. A, 134* (1931) 385.