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Thermodynamic and experimental study of CVD of non-stoichiometric titanium nitride from $TiCl_4$–N_2–H_2 mixtures

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Using the polynomial description of the Gibbs free energy of formation of titanium nitride against its composition, thermodynamic deposition diagrams were determined at 1900 K. The description of the whole range of non-stoichiometry needs $X\mathrm{TiCl_4} < 10^{-2}$ and $X\mathrm{N_2}$ as low as 10^{-4}. Deposition rates and composition of the film were studied. The cold wall reactor is associated with a dew point evaporator. At 1900 K, on a molybdenum substrate, experiments carried out as a function of input nitrogen, temperature and pressure, confirmed the theoretical trends. The different deposition mechanisms in relation to total pressure are thermodynamically related with a progressive reduction of the halide to solid titanium under one atmosphere instead of a major formation of gaseous titanium under 6.6×10^{-3} atm. The lowest N/Ti value obtained in the deposits is 0.63.

1. Introduction

The deposition of TiN has been reported under various conditions in many technical publications. As examples TiN films were deposited on refractory hard materials [1–5] and on steels [6–8], either by classical CVD or ultrasonic assisted CVD to achieve a better adhesion to the substrate [7]. The specific properties of such layers (hardness, wear and corrosion resistance) in association with an attractive colour are the stimulus for many industrial purposes. In spite of the considerable interest in the development of hard coatings, the studies do not pay attention to the composition of the deposited layer.

Since the properties of titanium nitrides ($Ti_{1-x}N_x$) depend to a large extent on their stoichiometry (from $X_N = 0.5$ to $X_N = 0.3$) it is of interest to know if the CVD technique is an appropriate way of producing layers of non-stoichiometric refractory compounds.

This paper deals with the investigation of the influence of the deposition conditions on the coating composition at high temperature using $TiCl_4$, N_2, H_2 mixtures.

2. Thermodynamic calculations

It is well known that an *a priori* complex equilibrium calculation is a useful approach to CVD problems. Many papers present such studies but few are devoted to chemical equilibria in systems composed of a gas phase and non-stoichiometric condensed phases. Several examples have been presented in the recent past [9–12].

Teyssandier *et al.* [12] calculated isocomposition curves of $Ti_{1-x}N_x$ in relation to the input gas phase ($X\mathrm{TiCl_4} + X\mathrm{N_2} + X\mathrm{H_2} = 1$ atm) at 1900 K. This deposition diagram was performed using a Gibbs energy minimization program in which only the analytical representation of the Gibbs energy of formation of the fcc $Ti_{1-x}N_x$ (δ phase) was introduced and the hcp (α) and bcc (β) phases were not considered due to lack of data. This procedure led to a boundary in the deposition field inconsistent with the phase diagram.

In a second step, using the known titanium–nitrogen phase diagram boundaries (α from $X_N = 0.12$ to $X_N = 0.23$, β between $X_N = 0$ and $X_N = 0.06$) thermodynamic data were estimated [13]. Thus this set of the integral Gibbs free energies of formation of the three solid solutions allows the calculation of a complete deposition diagram at 1900 K.

The gaseous species introduced were TiCl, $TiCl_2$, $TiCl_3$, $TiCl_4$, HCl, Cl_2, Cl, H_2, H, N_4H_2, N_2H_2, NH_3, NH_2, NH, N_2, N and the condensed ones Ti, $TiCl_2$, TiH_2, α, β, δ. The thermodynamic functions used for the solid solutions are summarized in Table I. All other values come from the SGTE data bank (Scientific Group Thermodata Europe) leading to the following features.

Figs 1 and 2 show the different deposition domains calculated under total atmospheric pressure (classical CVD) and reduced pressure (LPCVD), respectively.

The nitrogen to titanium ratio in the deposit increases with the input nitrogen content in the gas. It is worth emphasizing that the stoichiometric composition cannot be theoretically obtained as $X\mathrm{N_2}$ is always less than 1 atm. Under the investigated conditions for high $TiCl_4$ input partial pressures, a field in which no deposition occurs is observed. Figs 1 and 2 reveal that a decrease in total pressure tends to extend slightly the homogeneous gas equilibrium region and lower the highest nitrogen content available in the δ phase. Fig. 3 illustrates the simultaneous influence of the nitrogen input content and the total pressure on

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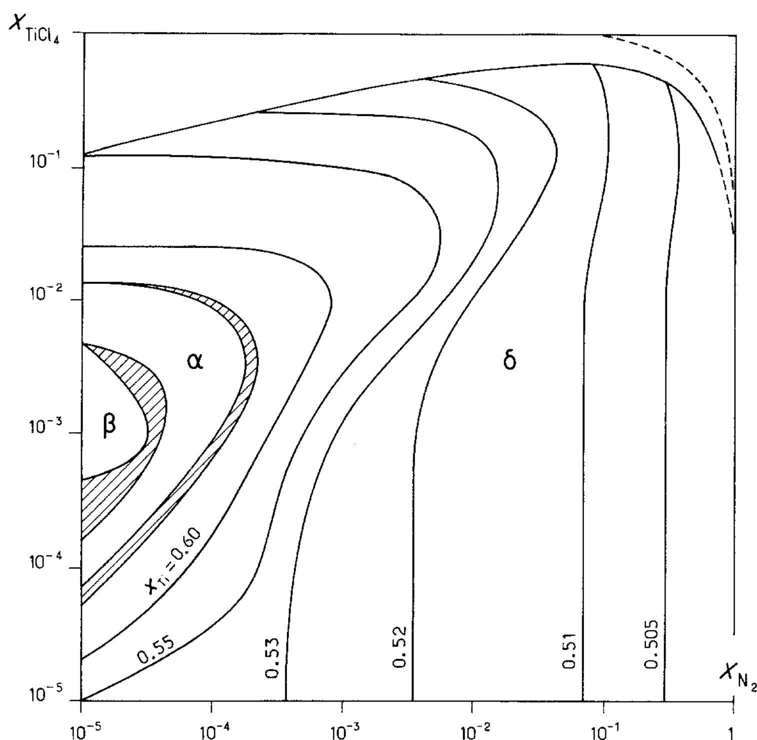

Figure 1 Deposition diagram calculated at 1900 K, under atmospheric pressure.

the composition of the solid solution ($\langle X_N \rangle$). These data show that the composition changes drastically when XN_2 is low ($< 3 \times 10^{-3}$) under atmospheric pressure. Furthermore, a low total pressure tends to soften the variation of the solid solution composition and to favour departure from stoichiometry for $XN_2 > 10^{-3}$.

To sum up, almost all the possible compositions of the δ phase can be theoretically obtained from $TiCl_4$, N_2, H_2 mixtures by variation of the nitrogen content in the gas phase if the initial molar fraction of $TiCl_4$ is low enough ($TiCl_4 < 10^{-2}$). Due to the shape of the deposition domains, the greatest departure from stoichiometry in the deposits is achieved close to $XTiCl_4 = 4 \times 10^{-3}$ for the largest input nitrogen content ($XN_2 \sim 2 \times 10^{-4}$). This value is related to the maximum deposition rate of titanium from the Ti–Cl–H system [14]. Thus, selecting this halide molar fraction and progressively increasing XN_2 in the gas phase from 10^{-4} is probably the best way to obtain the whole homogeneity range of the δ nitride either under atmospheric or reduced pressure.

3. Experimental procedure

A classical inductively heated vertical cold wall reactor was used to coat small slabs (diameter 16 mm, thickness, $e = 0.3$ mm). The gaseous mixture enters the reactor at the bottom. In order to avoid the formation of a carbonitride phase, graphite was not used as a substrate and the coatings were carried out at 1900 K on molybdenum which does not form stable nitrides above 1300 K. A micropyrometer was used for temperature measurements. Corrections of surface emissivity ($\varepsilon_{0.65} = -7.5 \times 10^{-5} T(\mathrm{K}) + 0.46$) [15] and transmission through the windows were applied.

The permanent gas flows are driven by mass flowmeters: N_2(99.995%) ranges from $50\,\mathrm{cm^3\,h^{-1}}$ to $1200\,\mathrm{cm^3\,h^{-1}}$ and H_2 (purified by diffusion through palladium) is fixed at $30\,\mathrm{l\,h^{-1}}$. To ensure a reliable, low, constant partial pressure of $TiCl_4$, a dew point evaporator was used.

Fig. 4 represents the results of a chemical calibration of $TiCl_4$ amounts carried away by hydrogen ($d = 30\,\mathrm{l\,h^{-1}}$) for different experimental values of the temperature of the column, taking into account the Grandage's vapour pressure relation [16]: $\log P_{\mathrm{torr}} = 6.79094 - (134.56)/(T_{\mathrm{^\circ C}} + 208.52)$, which fits the experimental results of several authors in different temperature ranges. For $TiCl_4$ partial pressures ranging from 4×10^{-3} to 10^{-2}, the carrier gas is almost saturated.

The weight increase was measured and the composition of the coatings was determined by X-ray diffraction on the surface. The lattice parameter, as shown by previous authors on pure materials (less than 0.1 wt % of oxygen or carbon), exhibits a linear

TABLE I Thermodynamic data of the $Ti_{1-x}N_x$ phases at 1900 K ($\mathrm{cal\,mol^{-1}}$)

$\Delta G \langle Ti_{1-x}N_x \rangle = x(1-x)[ax^4 + bx^3 + cx^2 + dx + e] + RT[x\mathrm{Ln}x + (1-x)\,\mathrm{Ln}\,(1-x)] + (1-x)\,\mathrm{A} + x\mathrm{B}$

Ref. Ti_{cc}, $N_{2_{gaz}}$

Phase	a	b	c	d	e	A	B
δ	10 421 415	−13 195 179	5 949 507	−1 220 466	0	27 919	470
β	0	0	−110 674	67 841	−90 212	31 285	0
α	0	0	−154 714	−54 473	−135 557	75 298	670

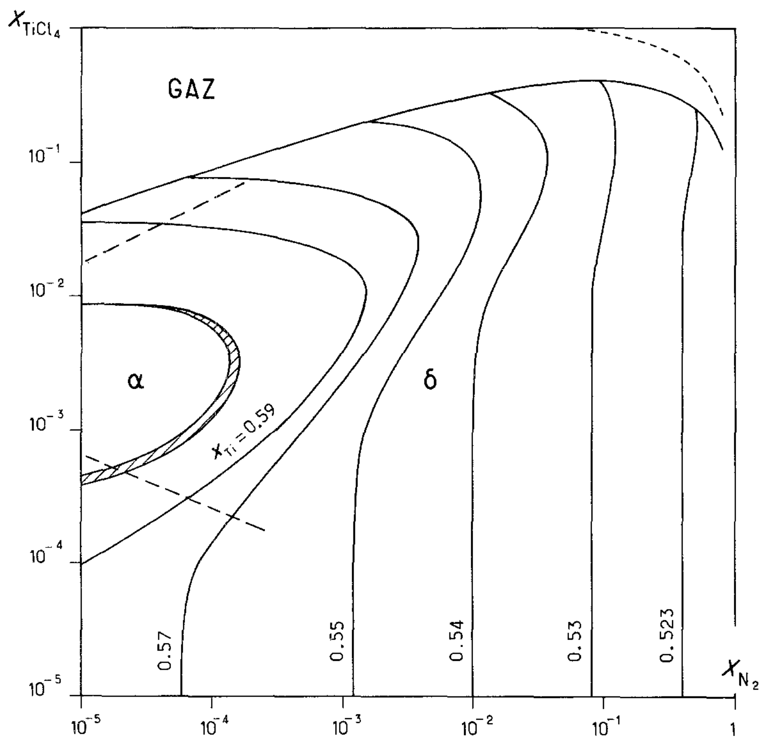

Figure 2 Deposition diagram calculated at 1900 K, under 5×10^{-3} atm.

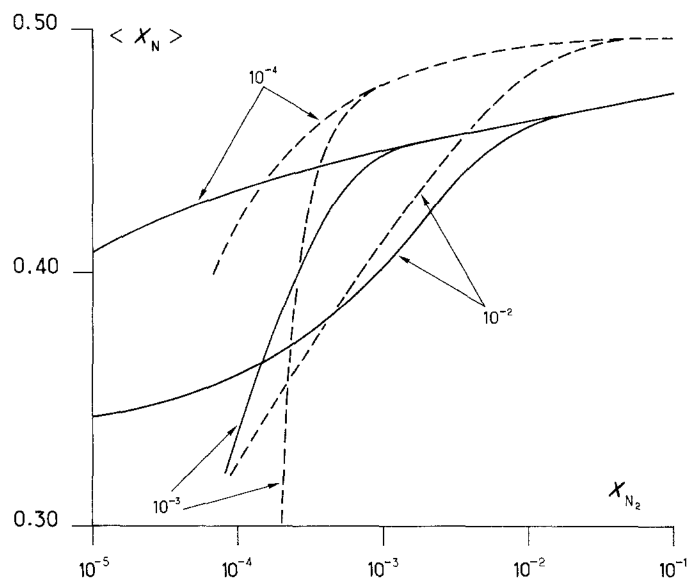

Figure 3 Composition of the solid solution against input partial pressure of N_2 for different $TiCl_4$ contents. ---, total pressure 1 atm; ——, total pressure 5×10^{-3} atm.

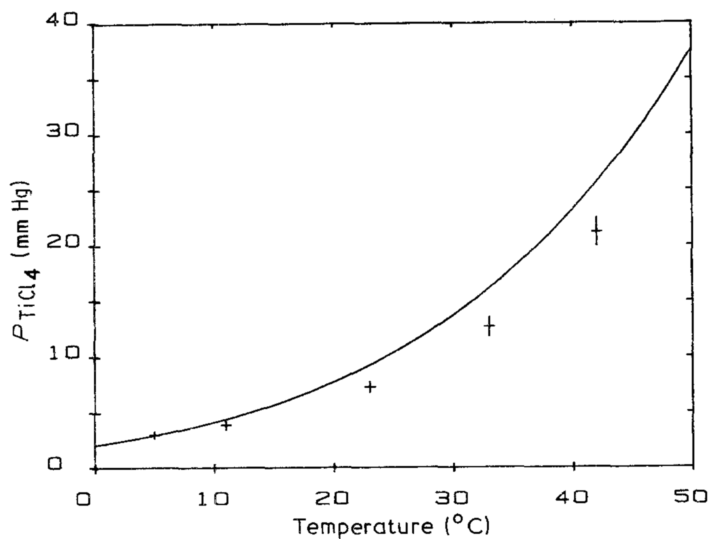

Figure 4 Calibration of the dew point evaporator.

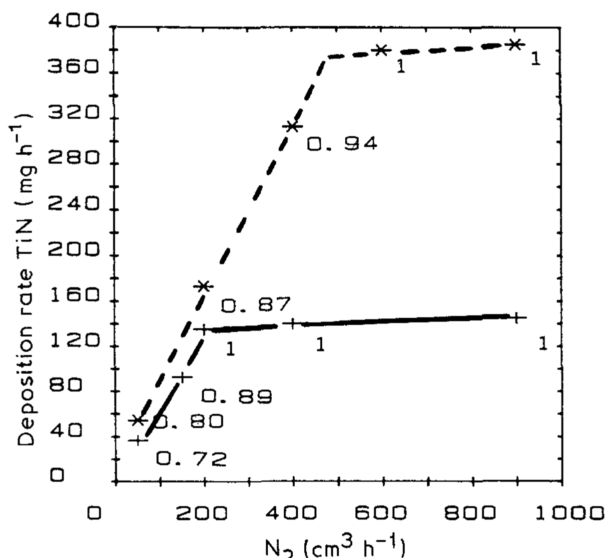

Figure 5 Deposition rate at 1900 K, P = 1 atm against input N_2 flow rate. ——, Input $TiCl_4 = 4 \times 10^{-3}$ atm; – – –, input $TiCl_4 = 10^{-2}$ atm.

variation with the nitrogen to titanium ratio $a\,\text{nm} = 0.41925 + 0.00467\,\text{N/Ti}$ [17]. This relationship fits different experimental data well [18, 19].

The influence of total pressure, input content of nitrogen and temperature was also examined.

4. Results and discussion

The influence of the N_2 input content at 1900 K is presented in Fig. 5 for $X\text{TiCl}_4 = 4 \times 10^{-3}$ and 10^{-2} with respect to the composition of the deposits under atmospheric pressure. The growth rate seems to be controlled by the nitrogen partial pressure until stoichiometry is reached, after which it becomes constant.

For $N_2 = 50\,\text{cm}^3\,\text{h}^{-1}$ resulting in a N/Ti ratio of 0.72, a scaling effect occurs systematically when the sample is cooled; in these circumstances, the remaining weight of the sample can be lower than the initial one which means that some molybdenum has diffused towards the deposit. As this was not observed for higher N/Ti values it may be thought that diffusion with the substrate is enhanced by departure from stoichiometry. Under reduced pressure the deposition rate behaves differently; its value is lower, the departure from stoichiometry greater and N/Ti = 1 is never reached. It also depends closely on the N_2 content in the whole investigated range, implying that this gas is probably a minor component at the gas–solid interface despite its excess compared with the halide partial pressure in the input gas phase. Furthermore as shown by Fig. 6, diffusion between the substrate and the deposit is suppressed under low total pressure (6.6×10^{-3}).

A comparison of the experimentally determined N/Ti ratio against N_2 content and the calculated values under atmospheric pressure is plotted in Fig. 7. Stoichiometry is experimentally reached for input $X\text{N}_2/X\text{TiCl}_4 = 1.6$, which is not the case under reduced pressure for input nitrogen content as large as 4×10^{-2}.

The lowest theoretical ratio N/Ti = 0.41 ($Ti_{0.71}N_{0.29}$) may not be obtained due to the difficulty of achieving very low nitrogen flow rates and the probable limitation by diffusion with the molybdenum substrate. This latter assumption is based on the fact that in the experimental deposition of titanium carbide onto molybdenum, the lowest solid solution composition $Ti_{1-x}C_x$ is governed by the Ti–Mo–C phase diagram and is in good agreement with it [20]. This cannot be checked here because of a lack of data on the TiMoN system and difficulties of carrying out a microprobe analysis due to the overlapping of the titanium and nitrogen peaks. Nevertheless one can say that the theoretical trend is verified with a slight shift which seems to be weaker under 6.6×10^{-3} atm.

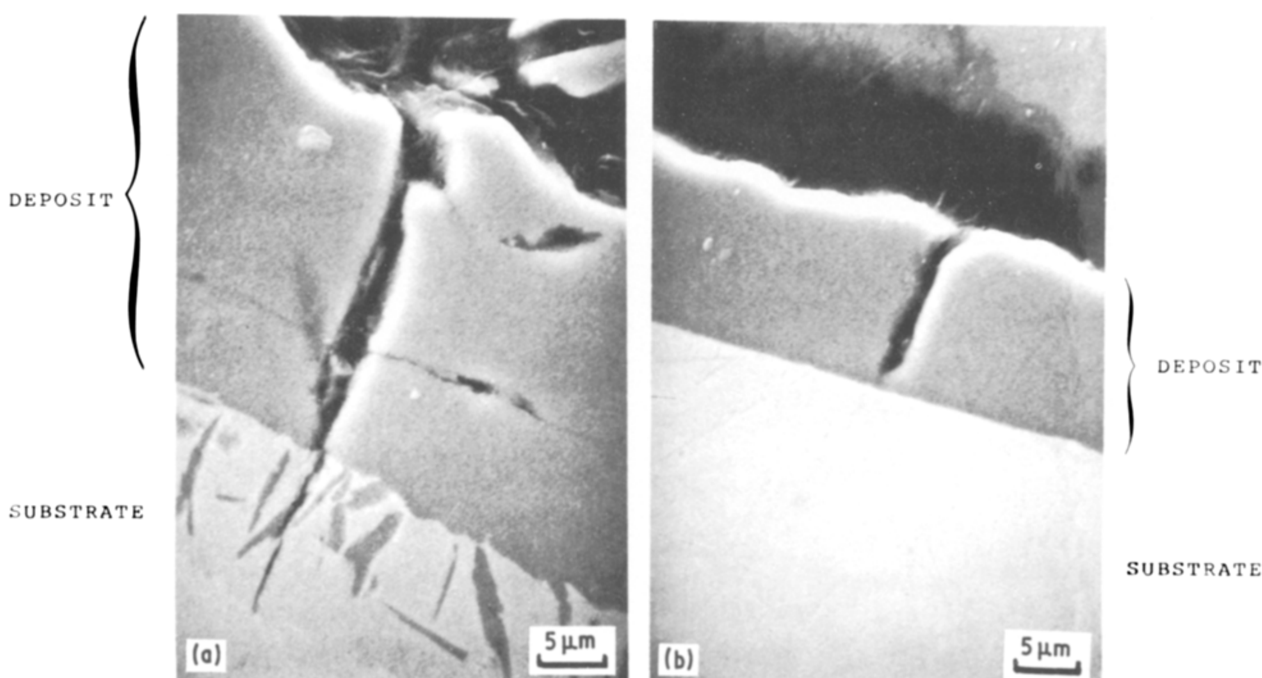

Figure 6 Cross sections of samples prepared at (a) 1 atm, (b) 6×10^{-3} atm (T = 1900 K; D = 30 l h^{-1}).

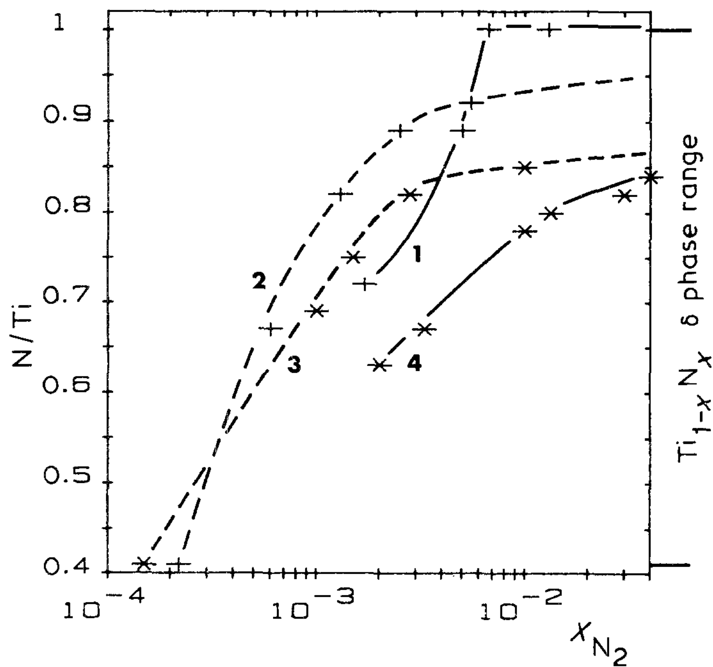

Figure 7 Composition of the deposit against input nitrogen for T = 1900 K, $X TiCl_4$ = 4 × 10^{-3}. ——, Experimental; – – –, theoretical. (1, 2) 1 atm; (3, 4) 6 × 10^{-3} atm.

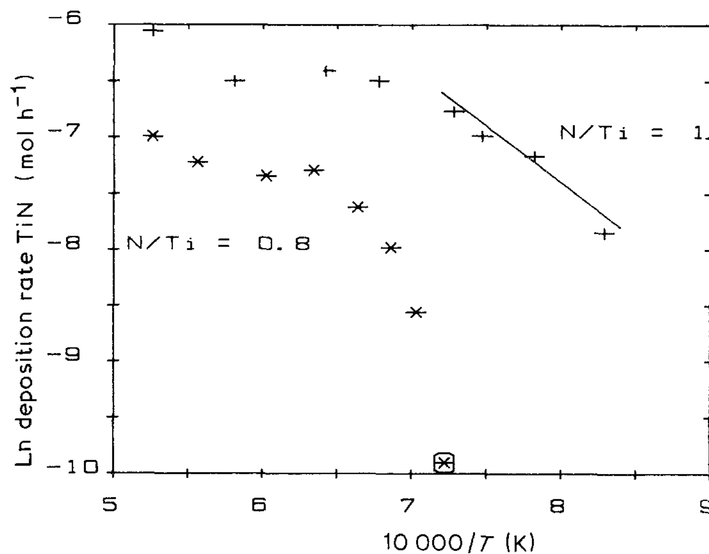

Figure 8 Deposition rate against temperature. +, total pressure 1 atm; ∗, total pressure 6 × 10^{-3} atm.

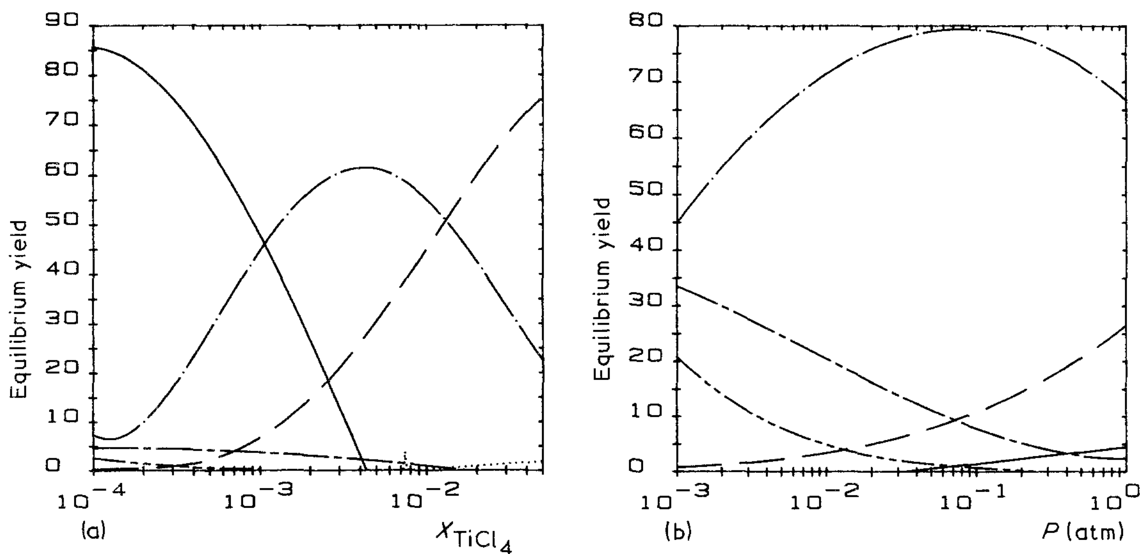

Figure 9 Thermodynamic efficiencies of the titanium species in the Ti–Cl–H system at 1900 K. (a) against $X TiCl_4$ under atmospheric pressure; (b) against pressure for $X TiCl_4$ = 4 × 10^{-3}. ——, Ti (S); - - - -, Ti (G); – – –, TiCl; · · · ·, $TiCl_4$; — — —, $TiCl_3$; —·—·—, $TiCl_2$.

For the gas phase composition leading to the richest composition in nitrogen, that is $X\text{TiCl}_4 = 4 \times 10^{-3}$, $X\text{N}_2 = 3 \times 10^{-2}$, the deposition rate was studied against temperature. Its behaviour in the range 1200–1900 K is presented in Fig. 8. Under atmospheric pressure an activation energy of 20 kcal mol^{-1} can be deduced on the low temperature side. Under reduced pressure the deposition rate seems to increase more smoothly and is always lower.

The above results show that when total pressure is decreased stoichiometry is no longer obtained:

1. Diffusion with the substrate is not observed.
2. The deposition rate decreases.

Thus it may be thought that a change in the mechanism with total pressure is involved. Such an assumption is consistent with the deposition rate variation since the general feature associated with a mass transport-control (increase of deposition rate as pressure decreases) is not observed; and is also consistent with the thermodynamics of the Ti–Cl–H system which suggest an explanation.

Under atmospheric pressure, equilibrium calculations indicate a progressive reduction in the gas phase $TiCl_3$, $TiCl_2$, Ti leading to the formation of solid titanium [14] depending on the initial $TiCl_4$ content (Fig. 9a). Such an evolution is in agreement with mechanisms in which the formation of titanium nitride undergoes an intermediate step involving adsorption of solid titanium and nitrogen to the surface [21].

Under reduced pressure (6.6×10^{-3}), for the input $TiCl_4$ molar fraction corresponding to the theoretical maximum deposition yield, the equilibrium composition is completely different as shown in Fig. 9b. The amount of gaseous titanium becomes greater and a reaction between adsorbed nitrogen and gaseous titanium may be assumed.

In conclusion, it is possible to control the amount of nitrogen lattice vacancies in titanium nitride by adjusting the nitrogen content in the input gas phase $TiCl_4$–N_2–H_2. Under reduced pressure, the deposition mechanism is modified. In this case the formation of gaseous titanium can explain the lack of interdiffusion with the substrate.

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