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Thermodynamic simulation of atmospheric DLI-CVD processes for the growth of chromium-based hard coatings using bis(benzene)chromium as molecular source

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A B S T R A C T

Direct liquid injection (DLI) is a new technology particularly convenient for feeding CVD reactors with low volatility molecular precursors. Thus DLI-CVD can operate under atmospheric pressure and is a promising process for industrial applications requiring high precursor flow rates such as continuous deposition. In order to help the experimenter, a thermodynamic approach is particularly suitable for determining the chemistry of the process, i.e. the influence of the main growth parameters such as temperature, total pressure and initial gas phase composition on the nature of the deposited phases. A choice of the most explicit representations of the thermodynamic modelling describing the great trends resulting from the variation of experimental parameters is presented. Thermodynamic calculations in the Cr–C–H, Cr–N–C–H and Cr–C–Cl–H chemical systems were made to predict the atmospheric CVD growth of carbides, nitrides and metal chromium coatings, respectively. Bis(benzene)chromium (BBC) was used as metalorganic precursor and the calculations simulated respectively the reactive gas phase mixtures BBC/solvent, BBC/NH₃/solvent and BBC/C₆Cl₆/solvent. Even if a satisfactory agreement was found between experimental and theoretical tendencies, the deposition of metastable phases reveals that kinetics can play a major role in such processes. Based on these results, chromium carbides, nitrides and metal coatings have been successfully deposited by DLI-CVD under atmospheric pressure either as single phased or nanostructured multilayer hard coatings.

Keywords

Thermodynamic
Kinetic
CVD modelling
Data bases
Chromium based coatings
Bis(benzene)chromium

1. Introduction

More than fifteen years after our previous work on MOCVD of Cr-based hard coatings starting from bis(benzene)chromium (BBC) as Cr source [1–3], the launching of recent projects on nanostructured metallurgical coatings gave us the opportunity to take stock the situation in two particular fields: (i) the thermodynamic approach of the CVD process using critical data bases and, (ii) application of this approach to the new deposition method DLI-CVD that involves a great amount of vapor of hydrocarbon solvent and that can operate under atmospheric pressure. Indeed this process was used for the growth under atmospheric pressure of Cr-based nanostructured multilayer hard coatings. Experimental details and the main results are reported in A. Douard's PhD thesis [4] and will be published, topic by topic, in parallel papers. The goal of the present paper is to show through consistent examples originating from this PhD work that thermodynamic modelling is a useful method to develop new CVD processes and to discuss the limit when advanced coatings are deposited.

2. Previous works and new developments

2.1. Developments in thermodynamic modelling and data bases

The perfect data base doesn't exist and it is well known that there is continuous improvement of the data. Therefore, our recent work [4] was a good occasion to illustrate the weight of the changes that were realised between 1990 and 2008 concerning the results of our thermodynamic modelling.

To simulate deposition reactions, free energy minimisation software systems use models to represent this function, and data bases provide the model parameters. While the thermodynamic models [5] developed during the 70s and 80s have been refined in recent years, their structure has not been modified. Data bases such as those of the SGTE [6] are, for their part, being continually improved. Two types of files are consulted for the calculations: (i) files of the solution database and (ii) files of pure substance database (including gases).

Regarding phase solutions, the deposition experiments studied concern essentially the low-temperature isothermal sections of the C–Cr–1/2 N₂(g) diagram. Since 1990, no new experimental studies on the phase equilibria involved in this high-temperature system have been undertaken. Consequently, the only experimental results available are those of P. Ettmayer [7,8] between 1273 and 1673 K, results that have been used to adjust our parameters for the Cr₂(N,C)

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hcp A3 ternary phase based on a simple model known as the Redlich-Kister model [9]. Concerning the parameters of the Cr - N and Cr - C binary systems, they were drawn from [10] and [11] respectively which were then selected in the SGTE [6] bank. For the Cr(N,C) fcc A1 phase, the substitution of C atoms on the N lattice was not envisaged since the phase did not appear in the high-temperature experimental ternary section. The extension of the low-temperature model gave the isothermal section reproduced on Fig. 1a [1,2]. Since then, based in particular on unpublished work by P. Gustafson, the SGTE has carried out the complete modelling of the system by describing the hexagonal ($\text{Cr}_2(\text{N,C})$ hcp A3) and face-centred cubic ($\text{Cr}(\text{N,C})$ fcc A1) ternary phases by a sub-lattice formalism [12]. When used with the SGTE 2006 data base, this model leads to a low-temperature isothermal section which differs from the previous one mainly by the presence of the $\text{Cr}(\text{N,C})$ fcc A1 phase and the tie lines connecting the carbon-rich carbide and the $\text{Cr}(\text{N,C})$ fcc A1 nitride phases, indicating that they are in equilibrium at 800 K (Fig. 1b). This last point is important since it predicts a good thermodynamic stability of interfaces in nanostructured multilayer CrN/Cr_x coatings. These SGTE 2006 data were used to model our deposition experiments.

On the gas phase side, the data selected are taken, as before [1-3], from the SGTE file of pure substance database. The only difference concerns the BBC gas. In the previous study [1-3], the molecule was assumed to be completely decomposed at the substrate level and the corresponding stoichiometric mass balance was injected in the calculation. In this study, the thermodynamic parameters of the gas-phase BBC were established from the enthalpy of formation of 243.3 kJ/mol selected by the NIST data base and by smoothing of the specific heats and the absolute entropy measured by J.T.S. Andrew et al. [13]. The calculations reveal that taking this thermodynamic description into account does not make any modification. This means

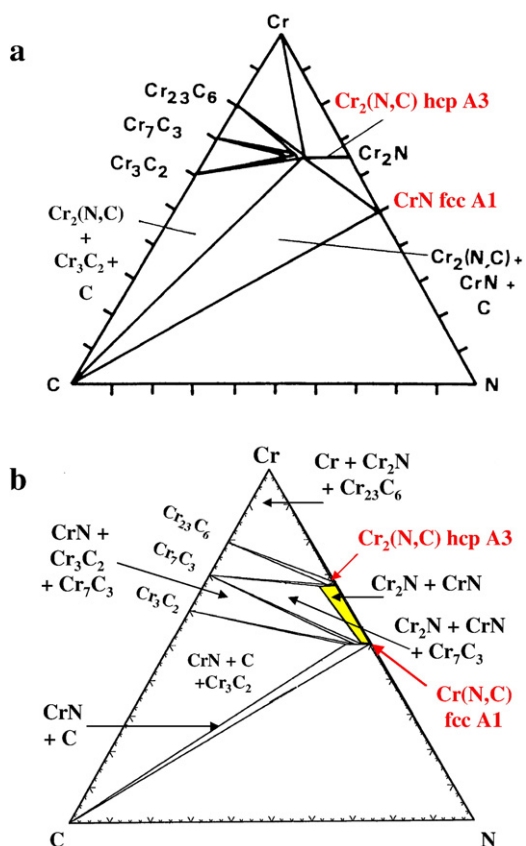


Fig. 1. Calculated isothermal sections of the Cr-N-C system at 800 K: (a) after Schuster et al. [1,2], (b) using the new data base (this work).

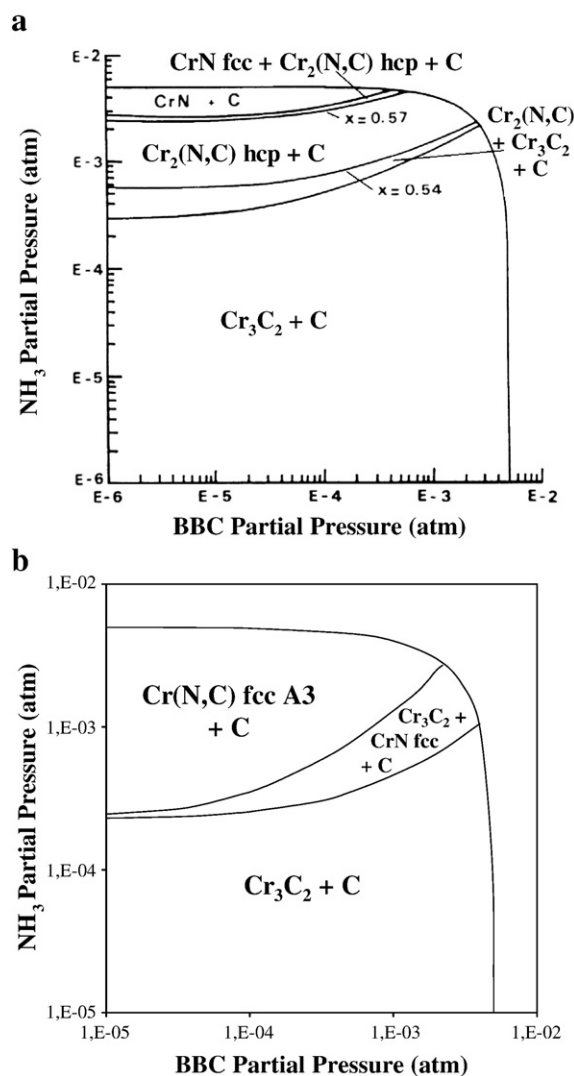


Fig. 2. Calculated deposition diagrams simulating the use of the reactive gas phase mixture BBC/NH₃/He (or Ar) at 800 K under a total pressure of 5×10^{-3} atm: (a) after Schuster et al. [2,3], (b) using the new data base (this work).

that, at the deposition temperatures used, according to the initial hypotheses [1-3], the BBC molecule decomposes completely in agreement with later experimental observations [14].

Before modelling the current deposition experiments carried out under atmospheric pressure, and in order to gain a better idea of the impact of the new data, the CVD diagram corresponding to the BBC - Ar - NH₃ mixtures used under a total pressure of 5×10^{-3} atm at 800 K previously calculated and shown on Fig. 2a [1,2] was recalculated with the present data. The new CVD diagram is presented on Fig. 2b. The major differences are the disappearance of the $\text{Cr}_2(\text{N,C})$ hcp A3 phase and the extension of the $\text{Cr}(\text{N,C})$ fcc A1 phase domain.

2.2. Development of deposition processes: DLI-CVD

For the growth of metallurgical coatings, there is an increasing interest for atmospheric pressure CVD as alternative to either vacuum techniques or deposition processes that use toxic solutions. For instance APCVD is attractive for on-line strip coatings on steel. In that case two key points have to be overcome: (i) a sufficiently low deposition temperature, which is achieved using metalorganic precursors and (ii) a high growth rate, which can be satisfied using high flow rates of precursor. However, although chromium carbides and nitrides coatings have been grown by low pressure CVD using metalorganic

precursors, these Cr sources are generally solid compounds with a relatively low vapor pressure, which did not permit to develop reliable atmospheric CVD processes [15,16]. Direct liquid injection is a new technology particularly convenient to feed the CVD reactors with high flow rates of precursor exhibiting a poor volatility. It has been developed principally for the growth of functional oxide thin films [17]. DLI-CVD can operate under atmospheric pressure and it was also used for the deposition of Cr-based coatings [18].

In this work, bis(benzene)chromium (BBC) was used as Cr source and toluene as solvent. The liquid solution was injected in a DLI-CVD reactor previously described [18] and the process conditions are detailed elsewhere [4].

3. Results

To illustrate the benefits of thermodynamic simulation, some significant examples are given to comment the effect of key deposition parameters when different gas mixtures are used. Various representation methods of the results are shown. These examples are taken from the PhD work of A. Douard [4]. An exhaustive presentation of the results obtained by modelling the numerous experiences that were realised [4] would be too long and has to be published chemical system by chemical system. Therefore, we have selected here the more explicit types of calculated diagrams in order to illustrate the great trends resulting from the variation of experimental parameters.

3.1. Chromium carbide coatings: Cr - C -H system

In order to assess the possibility of depositing different chromium carbides, it is important to know the influence of the parameters at the experimental worker's disposal concerning the existence and extent of the deposition domains of these carbides obtained using a BBC-Ar-H₂-solvent input gas mixtures. The initial calculation conditions are focused on the experimental conditions, namely: atmospheric pressure, temperature between 723 and 823 K, 10⁻⁴ mol of BBC, and

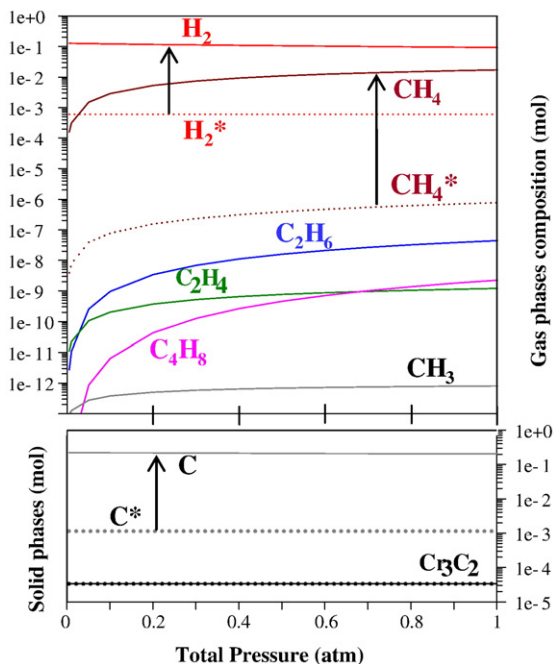


Fig. 3. Calculated composition of the gas and solid phases versus the total pressure for the Cr-C-H system simulating the decomposition at 773 K of BBC/Ar mixtures with and without toluene as solvent. The data without solvent are labeled with an asterisk (dotted lines). Initial BBC concentration = 10⁻⁴ mol; toluene = 3.15 · 10⁻² mol; total mole number = 1.

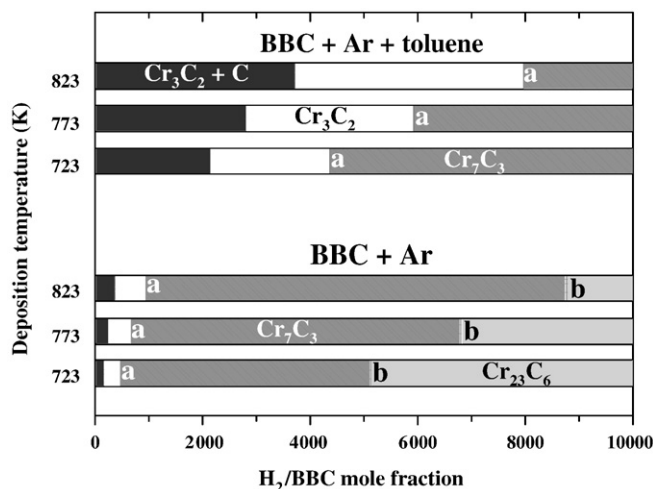


Fig. 4. Theoretical stability domains of the solid phases as a function of the temperature and the H₂/BBC mole fraction ratio without and with toluene as solvent. A very narrow biphasic domain exists at the position marked (a) Cr₃C₂+Cr₇C₃ and (b) Cr₇C₃+Cr₂₃C₆. Calculation performed for a total pressure of 1 atm under Ar ambient (initial BBC concentration = 10⁻⁴ mol; toluene = 10⁻² mol; total mole number = 1).

total initial number of BBC, Ar, H₂ and solvent moles equal to 1. The thermodynamic simulation, indicated on Fig. 3, is used to analyse the effect of total pressure and of the solvent both on the gas-phase composition and on the nature of the deposited phases. It is well admitted that working under atmospheric pressure is advantageous with respect to experimental costs. Modelling also shows that it is favourable, with or without solvent, since it leads to a reduction in the co-deposited carbon, which is removed to the gas phase as CH₄. This effect is significantly accentuated in presence of toluene (solvent).

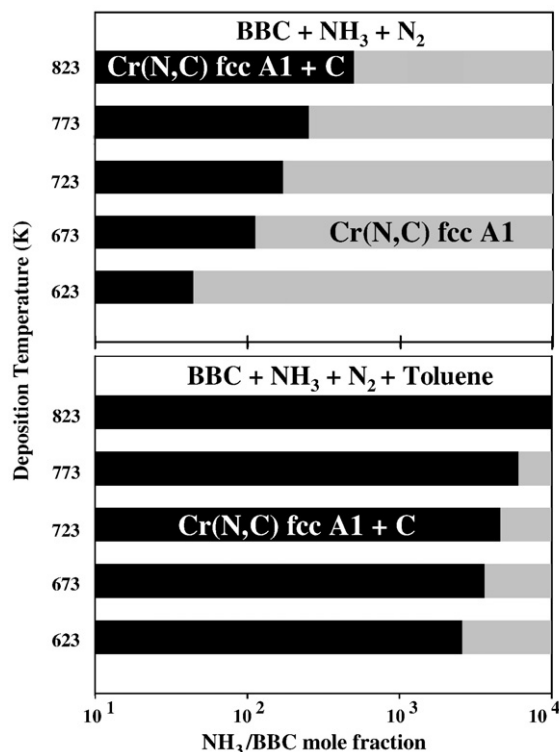


Fig. 5. Theoretical stability domain of the solid phases as a function of the deposition temperature and the NH₃/BBC mole fraction ratio without and with toluene as solvent. Calculation performed for a total pressure of 1 atm under N₂ ambient (initial BBC concentration = 10⁻⁴ mol; toluene = 3.15 · 10⁻² mol; total mole number = 1).

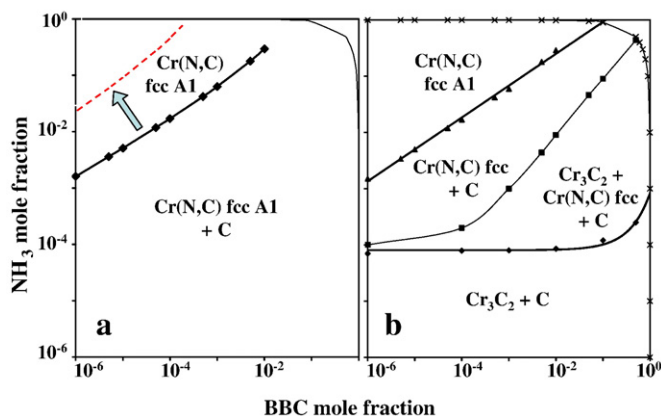


Fig. 6. Deposition diagrams calculated at 773 K for a total pressure of 1 atm simulating the use of reactive gas phase mixtures without solvent: (a) BBC/NH₃/N₂; (b) BBC/NH₃/Ar. The dotted line shows the influence of toluene: when it is present it shifts the boundary and decreases the single phased domain of the Cr(N,C) fcc.

Another example of using the simulation results is given on Fig. 4, where the following effects can be analyzed simultaneously:

- the temperature effect: with or without solvent, an increase in temperature leads to carbide deposits that are increasingly carbon-rich,
- the effect of a hydrocarbon solvent: the influx of a large number of carbon atoms for a constant number of chromium atoms leads to the formation of carbon-rich carbides,
- the hydrogen dilution effect: the carbon enters the gas phase in the form of hydrocarbon molecules and therefore leads to the formation of carbide deposits richer in chromium.

3.2. Chromium carbonitride coatings: Cr - N - C - H system

With the aim of depositing chromium carbonitrides, BBC - N₂ - NH₃ - solvent gas mixtures have been used. As above, the initial calculation conditions are focused on the experimental conditions: atmospheric pressure, temperature between 623 and 823 K, 10⁻⁴ moles of BBC, and a total initial number of BBC, N₂, NH₃ and solvent moles equal to 1. CVD diagrams such as those shown on Fig. 2, must be established first, but other representation methods are also very useful. For example, a representation identical to that in Fig. 3 used for Cr-C-H system is drawn on Fig. 5 for Cr-C-N-H system. It describes the effects of temperature and NH₃/BBC dilution rate, with or without solvent (toluene in this case). The phases theoretically deposited at thermodynamic equilibrium are either a co-deposit of Cr(N,C) fcc A1 + C, or the Cr(N,C) fcc A1 ternary phase alone. Even if the real system is not at thermodynamic equilibrium, the trends revealed by these calculations will be still observed but with some shifts due to the kinetics.

In the absence of any detailed information on the kinetics of the reactions likely to occur on the substrate, it is in certain cases possible

to determine two limits within which the chemical system operates during deposition. This concept is illustrated on Fig. 6. One side shows the deposition diagram corresponding to the phases deposited from BBC/NH₃/N₂ as initial mixture injected into the reactor at thermodynamic equilibrium (Fig. 6a), while the other side gives the same diagram, but with Ar substituted for N₂. In our experiments N₂ is used as inert carrier gas, the active nitriding species being NH₃ as shown on Fig. 6b. At thermodynamic equilibrium, N₂ already behaves theoretically as an active species at working temperatures (773 K), which is not observed experimentally due to slow reaction kinetics. In modelling, to take into account artificially this extremely slow reaction kinetics, Ar is substituted to N₂. In this case, it is found that for the small quantities of NH₃ initially present, the Cr₃C₂ carbide can be co-deposited with the cubic ternary phase and carbon or with carbon alone. The experimental reality lies somewhere between these two extreme cases.

In summary, the great trends imposed by the evolution of experimental parameters (total pressure, initial reactants partial pressure, temperature or solvent effects) and predicted by thermodynamic modelling are really observed experimentally. Their knowledge is a considerable help for experimentalists and avoids long and costly trial and error methods.

4. Discussion: limits of thermodynamic modelling

The pure thermodynamic approach is not sufficient for a good modelling of the whole CVD processes. The following examples will show that, when kinetics are too complex or when deposited metastable phases are not included in the data base, or when a new chemical element appears (for instance due to contamination), it is not possible to correlate calculations and experiments.

Table 1 gives the experimental results as well as the nature of the phases that would be deposited if thermodynamic equilibrium were to be reached. As previously noted, while predicted trends remain accurate, the kinetic shifts can be quite considerable. This is particularly the case here in as much that the temperature is relatively low and the predicted free carbon deposit or co-deposit is always delayed by the slow kinetics, especially in quartz reactors.

4.1. Metal Cr coatings using the Cr-C-Cl-H system: complex kinetic and metastable phases

It is not always possible to describe the influence of kinetics without knowing the mechanism involved. For example, in previous experiments metallic Cr coatings were grown by MOCVD using BBC-C₆Cl₆-H₂-He gas mixtures under a total pressure of 6 Torr and at temperatures of the order of 673 K [14]. A thermodynamic calculation was not able to account for this observation which was at that time attributed to the slow decomposition kinetics of C₆Cl₆ [19]. Thus it was proposed that this molecule blocked the BBC adsorption sites thereby promoting the formation of metastable metallic chromium deposits containing a high percentage of carbon (10–15 at.%) at the expense of thermodynamically stable carbides. A reaction model based on additional mass spectrometry experiments

Table 1

Examples of problems encountered in the comparison between thermodynamic calculations and experimental data for various atmospheric DLI-CVD conditions using BBC/toluene solutions as Cr sources under N₂ ambient

Run no.	T (K)	Gaseous co-reactant	BBC mole fraction (ppm)	R/BBC ^(a)	Film XRD structure	Film composition (EPMA)	Phases predicted by thermodynamic modelling
24	723	-	71	0	Amorphous CrC _x	Cr _{0,69} C _{0,30} O _{0,01}	Cr ₃ C ₂ + C
25	773	-	66	0	Amorphous CrC _x	Cr _{0,69} C _{0,28} O _{0,03}	Cr ₃ C ₂ + C
30	773	C ₆ Cl ₆	130	1	Cr	Cr _{0,83} C _{0,17} O _{0,00}	Cr ₃ C ₂ + C
32	773	C ₆ Cl ₆	120	0.25	Cr	Cr _{0,85} C _{0,15} O _{0,00}	Cr ₃ C ₂ + C
33	773	C ₆ Cl ₆	115	0.1	Cr	Cr _{0,87} C _{0,13} O _{0,00}	Cr ₃ C ₂ + C
35	773	NH ₃	178	160	CrN fcc	Cr _{0,38} N _{0,29} O _{0,31} C _{0,02}	Cr(N,C) fcc A1 + C
36	773	NH ₃	200	280	CrN fcc	Cr _{0,40} N _{0,27} O _{0,31} C _{0,02}	Cr(N,C) fcc A1 + C
37	773	NH ₃	178	595	CrN fcc	Cr _{0,58} N _{0,15} O _{0,23} C _{0,04}	Cr(N,C) fcc A1 + C

^(a) Mole fraction ratio between the co-reactant (R) and BBC (R=C₆Cl₆ or NH₃).

was established in order to find results equivalent to those obtained in the experiments [14,19]. The present work conducted using BBC-C₆Cl₆-toluene-N₂ mixtures at 773 K under atmospheric pressure, produces the same coatings in spite of the presence of solvent and the increase of the total pressure (runs 30, 32, and 33 in Table 1). Modelling was performed based on the SGTE data base, notably with the Cr(C) bcc A2 solution which, in the Cr - C stable phase diagram, is found in extremely small quantities (C mole fraction always less than 0.01). Obviously, results equivalent to those found experimentally could not be obtained. The previous reactional model [14,19] can thus also be invoked.

4.2. Amorphous CrC_x phases

In the experimental runs 24 and 25, the deposits obtained are amorphous and since no data on metastable amorphous CrC_x are available, the calculation was not able to predict its formation. Predictive calculations of metastable phase deposits can be performed but the thermodynamic description still has to be evaluated [20].

4.3. Presence of a contamination element

In the experimental runs 35, 36 and 37, the Cr(N,C) fcc A1 phase deposited is in agreement with predictions, but the theoretical co-deposition of carbon is not observed. This carbon co-deposition is possibly kinetically delayed or, more probably, it is removed from the solid phase to the gas phase in the form of CO due to the presence of oxygen in the reactor. The origin of the oxygen is unclear at this stage (leak in the reactor, adsorbed H₂O on the reactor wall, purity of ammonia) but it is well known that CrN is very sensitive to oxidation and the composition of samples from the runs 35 to 37 confirms this last hypothesis.

5. Conclusion

Even for coatings for which the growth is strongly kinetically controlled, the benefits expected from a thermodynamic simulation of

the process will be invaluable for understanding and optimising the experiments. Moreover, the phase equilibria found in the new isothermal section represented on Fig. 1b are encouraging as they indicate that the CrN/CrC_x interfaces are thermodynamically stable. This indicates that it would be possible to make multilayer coatings with chromium carbides and nitrides without losing the nanostructuration which leads to enhanced properties.

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