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Vanadium Oxi-Carbide Coatings Deposited by OMCVD in an Isothermal Reactor

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Abstract. This paper reports on the influence of both the vaporization mechanism and gaseous transport phenomena, on the properties of vanadium oxi-carbide coatings. In order to study the influence of the residence time of the gaseous mixture on the properties of the deposited layer, a specific device has been built. In this device the temperature of the reactor wall is very accurately controlled to the vaporization temperature of the precursor by a heat pipe disposed inside a furnace, whereas the temperature of the substrate is imposed independently. A vacuum-tight sliding device allowed varying the length between the vaporization crucible and the deposition substrate. A complete factorial design with three factors and two levels, was carried out for two characteristic vaporization temperatures of the precursor. We studied the influence of three parameters on the thickness and composition of the deposits: the substrate temperature, the hydrogen flow rate, and the distance between the vaporization crucible and the steel substrate.

1. INTRODUCTION

Because of its high melting point and hardness as well as its good abrasion resistance and low friction behavior, vanadium carbide (VC) is a promising protective coating for steel pieces [1-3]. These coatings can be processed by Chemical Vapor Deposition (CVD). In the conventional thermally activated process, the initial gas mixture is composed of vanadium chloride, methane and hydrogen [4]. The temperature level required by the use of inorganic precursors, (in the range 1073 to 1473 K), is not compatible with the deposition on steel substrate. Such high temperatures are responsible for solid state reactions between the film and the substrate and cause residual stresses, grain growth of the substrate structure, stabilisation of the austenite structure, and decarburization of carbon-containing substrates. By the use of less stable molecules such as organometallic compounds CVD can be proceeded at much lower temperatures.

Literature dealing with CVD of vanadium carbide from such precursors is very scarce [5-7]. As reported in a patent [5], films containing vanadium and carbon have been obtained at low deposition temperatures (373 to 673 K) from several organometallic compounds: dicyclopentadienyl vanadium (or vanadocene), dicyclopentadienyl vanadium dichloride, dicyclopentadienyl vanadium dibromide, cyclopentadienyl vanadium tetracarbonyl, or dibenzene vanadium. This patent [5], suggests that vanadium carbide is only obtained above 973 K, whereas metallic vanadium is preferentially formed at low temperature. Recent investigations [6] confirmed that the pyrolysis at 973 K of a film deposited at 623 K from vaporized cyclopentadienyl vanadium tetracarbonyl (333-353 K, $V(Cp)(CO)_4$), results in the formation of vanadium carbide (V_4C_3). The initial low-temperature deposit was determined to be a polymeric cyclopentadienyl complex of vanadium [6]. Very recently, it has been shown that vanadium carbide can be deposited from vanadocene (Cp_2V , $Cp=C_5H_5$) at low deposition temperature (773-1123 K) [7,8].

In this study, vanadocene was used as a precursor of vanadium carbide at 773 K. This molecule which is easy to prepare with high yields and at low cost is not toxic and can be vaporized at relatively low temperature. Nevertheless, like most organometallic precursors, vanadocene is very moisture and oxygen sensitive and accordingly requires manipulation and storage in an inert-atmosphere.

Previous work have stressed the influence of the vanadocene vaporization procedure on the properties of the deposits [9,10]. As a matter of fact, according to the precursor vaporization temperature, the atoms necessary to grow the coating can be transported towards the substrate by means of an initially sublimated molecule, or by means of by-products resulting from its thermal solid state decomposition. Layers are

deposited from both vaporization procedures. Nevertheless, the difference in the nature of the gaseous species that are transported in the gas phase in each case, is responsible for different coating properties [9]. In a previous paper [10], we have shown that below 400 K the predominant vaporization process was the sublimation of Cp_2V , whereas above 400 K the solid state decomposition mechanism resulting from break of the central bond of the organometallic precursor prevailed. This paper is intended to determine the influence of both the vaporization procedure and the further transport of the reactive mixture on the properties of the coatings.

2. EXPERIMENTAL DETAILS

2.1. Chemical synthesis of Cp_2V

Vanadocene (Cp_2V) was prepared according to literature procedures [11-13] starting from Na (25 g; 1.08 mol), freshly cracked cyclopentadiene and VCl_3 (56.7g; 0.36 mol). All manipulations were carried out using high-vacuum line and Schlenk techniques. Tetrahydrofuran was purified from sodium benzophenone ketyl under argon and degassed before use. Sublimation of the crude product gave violet crystals of vanadocene (40g; 61% yield). The elemental analysis yielded: C:66.29; H:5.55 [calculated for $\text{C}_{10}\text{H}_{10}\text{V}$, (C: 66.31; H:5.56)]. The highly air and moisture sensitive product was loaded in an inert-atmosphere glove box and stored in sealed ampoules (1.5g loads) for further CVD experiments.

2.2. CVD configuration and procedure

In order to study the influence of the residence time of the gaseous mixture on the properties of the deposited layer, a specific device has been built (figure 1). In this device the temperature of the reactor wall was very accurately controlled to the vaporization temperature of the precursor, whereas a substrate temperature of 773 K was imposed independently for all experiments. The reactor was composed of a 60 cm long tube (ID = 38 mm) which was the inert part of a heat pipe disposed inside a furnace. This heat pipe allowed a maximum variation of the reactor wall of 1 K. The vaporization crucible loaded with 300 mg of Cp_2V was heated by contact with the reactor inert wall. It was covered by a lid with a 1 mm diameter hole drilled in the middle. The crucible was located at the entrance of the reactor, where the hydrogen carrier gas was admitted. Hydrogen flow rate was controlled and regulated to 15 l.h^{-1} or 30 l.h^{-1} by means of a mass-flow meter (ASM AFC 25). The substrate was disposed at the end of a cylindrical rod. A vacuum-tight sliding device allowed varying the length between the vaporization crucible and the deposition substrate in the range 5 to 50 cm. The films were deposited on steel substrates (steel reference 4135 from American Iron and Steel Institute, thickness = 0.5 mm, width = 5 mm). The steel strip had a specific shape that improved the length of the isothermal area and minimised the deformations induced by the thermal expansion. The substrate as well as the reactor temperatures were controlled by a chromel-alumel thermocouple connected to a PID regulator. A liquid nitrogen cooled trap attached to the reactor exhaust condensed unreacted precursor and by-products of the deposition.

The deposition surface of the steel substrates was polished metallographically using $1 \mu\text{m}$ diamond paste, sonicated and rinsed with freon. In order to prevent oxygen or water contamination, the precursor was loaded in part A of the deposition device (figure 1) in a glove box. The CVD system, loaded with the substrate and the precursor, was then evacuated for 12 h and purged with hydrogen for 30 min (30 l/h). The temperature of the reactor wall was heated from 298 K to the vaporization temperature of the organometallic precursor at a rate of 1 K/min. The crucible was then introduced inside the reactor by a vacuum-tight sliding device. A constant total deposition time of 300 min was imposed for each experiment. At the end of each experiment, heating of the crucible was stopped, and the temperature of the substrate was decreased gradually, with the hydrogen flow rate maintained until the substrate had reached room temperature.

Figure 1: Schematic of the CVD unit

2.3. Characterisation of the deposits

The thickness of the deposits was determined by the ball cratering method and SEM measurement on cross-sections. The elemental compositions of the deposits were measured on polished cross sections by electron probe microanalysis with wavelength dispersive spectroscopy (EPMA-WDS). The nature of the crystalline phases was determined by X-ray diffraction (XRD) using a copper anticathode. The surface morphology was observed both by optical microscopy and by SEM.

3. RESULTS AND DISCUSSION

3.1 Deposition study

Most of the experimental situations require the examination of the effects of varying two or more factors. It has been shown [14,15], that to obtain a complete exploration of such a situation it is not sufficient to vary one factor at a time, but all combinations of the different factor levels must be examined in order to elucidate the effect of each factor and the possible ways in which one may be modified by the variation of the others. A general useful procedure is provided by the factorial experiment method. When a restricted number of factors are considered, a response surface, which is the description of experimental results by a polynomial expression, can be determined by a multiple regression technique [16].

Among the numerous factors that may have significant influence on the deposition process, the temperature of vaporization of the precursor, T_p , the hydrogen flow rate, DH_2 , and the distance between the precursor handling crucible and the steel substrate, d , were selected according to previous results. The variation ranges of selected factors, which are defined by the lower and higher levels of the experimental design, are summarised in Table 1. An intermediate crucible-substrate distance level was added in order to provide a more accurate description of the influence of this factor. As a matter of fact, to estimate the coefficient of a degree n variable, at least $n+1$ levels of this variable are required in the experimental design. Consequently, the polynomial expression included linear dependence on the hydrogen flow rate (D) as well as for the vaporization temperature of the precursor (T_p), and linear and quadratic dependence on the distance between the precursor handling crucible and the steel substrate (d).

Level	-1	0	1
Substrate temperature T_s (K)	393	-	413
Hydrogen flow rate DH_2 (l/h)	15	-	30
Crucible - substrate distance d (cm)	5	34	50

Table 1: Experimental factors and corresponding levels used in the experimental design

3.2 Thickness

To provide an estimate of the standard deviation of the thickness measurement, three experiments were repeated for the same following conditions: $d = 50$ cm, $DH_2 = 30$ l.h⁻¹, $T_p = 393$ K. A mean value of 4.2 μm , and a variance of 0.07 were calculated from the measured thicknesses (4.1, 4.5, 4.0 μm). Therefore we assumed a standard deviation of 0.27 μm for the thickness reproducibility of the deposited coatings. The measured responses (coating thickness, composition) and the corresponding experimental parameters are presented in **Table 2**.

Sample	DH_2 (l.h ⁻¹)	d (cm)	T_s (K)	Thickness (μm)	Composition (at %)
1	15	5	393	5.9	V42.1C.5O57.4
2	30	5	393	5.5	V42.3C.4O57.3
3	15	34	393	5.3	
4	30	34	393	5.0	V41.8C.9O57.3
5	15	50	393	5.1	V42.0C.5O57.5
6	30	50	393	4.1	V42.3C.7O57.0
7	15	5	413	14.5	V41.9C.6O57.5
8	30	5	413	13.5	V42.2C.3O57.5
9	15	34	413	14.5	V42.7C.4O56.9
10	30	34	413	12.0	V42.4C.8O56.8
11	15	50	413	13.5	V42.5C.5O57.0
12	30	50	413	10.2	V42.5C.2O57.3

Table 2: Measured thicknesses and compositions of the coatings

The two following polynomial expressions were determined to represent the variations of the layer thicknesses within the experimental domain:

$$e(\mu\text{m}) = 5.17 - 0.17D - 0.51d - 0.11Dd + 0.02d^2 - 0.14Dd^2 \quad \text{for } T_p = 393 \text{ K} \quad (1)$$

$$e(\mu\text{m}) = 13.33 - 1.33D - 1.07d - 0.57Dd - 0.41d^2 - 0.26Dd^2 \quad \text{for } T_p = 413 \text{ K} \quad (2)$$

Figure 2a: Response surface of the coating thickness plotted as a function of the hydrogen flow rate (15-30 l/h) and the distance between the precursor and the substrate (5-50 cm). $T_p = 373$ K, $P = 1$ atm.

Figure 2b: Response surface of the coating thickness plotted as a function of the hydrogen flow rate (15-30 l/h) and the distance between the precursor and the substrate (5-50 cm). $T_p = 393$ K, $P = 1$ atm.

The two response surfaces drawn in figure 2a and 2b indicate that the three factors have a significant influence on the coating thickness. However, the vaporization temperature of the precursor is by far the most important. This influence was already pointed out in a previous work dealing with the thermal behavior of vanadocene [10]. Below 400 K, the predominant vaporization process is the sublimation of Cp_2V . In contrast, above 400 K a solid state decomposition of the molecule occurs that involves the break of the central bond. As a result, new chemical species are transported in the gas phase that are responsible for a different deposition mechanism and thus different coating properties. Complementary experiments carried out to estimate the deposition rate, furthermore stressed the critical influence of the vaporization procedure and the subsequent transport of the molecules in the OMCVD process (figure 3a). For $T_p = 393$ K, a linear deposition rate of $1 \mu\text{m}\cdot\text{h}^{-1}$ is observed that corroborates a pure sublimation process of the precursor. Instead, at $T_p = 413$ K the non linear variation of the coating thickness as a function of the deposition time can be explained by the time dependence of the amount of active species vaporized from the solid state decomposition.

Figure 3a: Variation of the coating thickness as a function of the deposition time (min).

Figure 3b: Variation of the coating thickness as a function of the gas phase residence time in the reactor (s).

As the transport parameters (d and DH_2) are two components of the gas phase residence time in the reactor, their influence will be discussed according to this parameter. In our case, the residence time is given by the following expression:

$$\tau = \frac{d \times S}{D} \times \frac{P_0}{P} \times \frac{T}{T_0}$$

where S is the surface section of the reactor, P and T the actual experimental pressure and temperature, T_0 and P_0 the standard temperature and pressure.

Though the actual residence-time should take into account the influence of the density variation of gases in the thermal boundary layer surrounding the hot substrate, we will neglect this influence and consider that the residence-time is, to a first approximation, proportional to d/D :

$$\tau = K \times \frac{d}{D}$$

Six different residence times are deduced from all the combinations of the d and DH_2 values used in the experimental design. The variations of the deposit thicknesses are presented in **figure 3b** as a function of the residence time.

In all cases, a linear dependence of the layer thickness on the crucible-substrate distance is observed for the various vaporization temperatures of the precursor and hydrogen flow rates. For the pure sublimation conditions at $T_p = 393$ K, the thickness is slightly decreasing when the crucible-substrate distance increases, and a weak influence of the hydrogen flow rate is observed. This behavior is indeed expected when the sublimated molecule is transported at a constant temperature corresponding to its vaporization temperature. Neither condensation, nor reaction in the gas phase are expected in this case. Due to the weak influence of the transport parameters on the layer thickness at $T_p = 393$ K, the thickness variation can be defined as a function of the residence time by the following expression:

$$e(\mu m) = 5.573 - .006 \tau(s) \quad (3)$$

For the vaporization conditions corresponding to the solid state decomposition of the precursor at $T_p = 413$ K, the influence of the hydrogen flow rate is clearly seen. At low hydrogen flow rate, the dependence of the layer thickness on the crucible-substrate distance is very similar to the behavior observed at $T_p = 393$ K. In contrast, at high hydrogen flow rate, the layer thickness decreases significantly when the crucible-substrate distance increases. This result stress the influence of the transport parameters in the case of large residence times of the gas phase that could be encountered in an industrial process.

3.2 Surface morphology

All the deposits exhibited a grey colour characteristic of vanadium oxy-carbide. The surface morphology, as revealed by SEM observations, is mainly dependent on the vaporization temperature of the precursor (T_p) and the hydrogen flow rate (DH_2), but the influence of the crucible-substrate distance (d) is very weak. The surface morphology presented in **figure 4a** is characteristic of the layers deposited at the low vaporization temperature of the precursor and presents a fine microstructure with crystal habits. Neither the crucible-substrate distance nor the hydrogen flow rate have significant influence on the surface morphology when the vanadocene molecule is sublimated. In contrast, when the precursor is decomposed in the vaporization crucible at 413 K, a coarser microstructure is observed whose size moreover increases with the hydrogen flow rate (**figure 4b** and **4c**). These observations provide once more evidence of the importance of the vaporization temperature of the precursor. When the precursor is sublimated, the microstructure is not modified by the transport parameters. Instead, as already observed for the growth rate, when the coating is grown from by-products resulting from the thermal decomposition of the organometallic molecule, the effect of hydrogen flow rate appears significant and reveals the importance of the gas phase transfer.

Figure 4a: characteristic surface morphology of layers deposited under sublimation vaporization conditions ($T_p=393$ K)

Figure 4b: characteristic surface morphology of layers deposited under decomposition vaporization conditions ($T_p=413$ K), for a hydrogen flow rate of 15 l/h.

Figure 4c: characteristic surface morphology of layers deposited under decomposition vaporization conditions ($T_p=413$ K), for a hydrogen flow rate of 30 l/h.

3.3 Composition

From the measured compositions reported in **table 3**, it is immediately obvious that all the coatings include a very low amount of carbon ($<1\%$ at) and conversely a high oxygen contamination content. On one hand such a low carbon content is surprising if we consider the composition of the initial precursor molecule ($C/V=10$). On the other hand, according to the ternary phase diagram V-C-O [17] and a thermodynamic study of the V-C-O system between 773 and 973 K [18], the thermodynamic stability of vanadium oxides as compared with the stability of vanadium carbides is increasing when the deposition temperature decreases. As a matter of fact, for the same experimental conditions, vanadium carbide including less than 1 at% oxygen contamination was obtained at a substrate temperature of 973K, but its deposition rate which was rather low at 973 K ($0.5 \mu\text{m}\cdot\text{h}^{-1}$) vanished at 873K. At a substrate temperature of 773K, these experimental conditions led to vanadium oxo-carbide layers with a deposition rate of $1.5 \mu\text{m}\cdot\text{h}^{-1}$ [9]. Therefore, no deposit would be obtained by chemical vapor deposition carried out at 773 K from vanadocene, in the absence of any oxygen source of contamination. The oxygen content of our layers (up to 57at%) is very high. Such a high oxygen contamination level is often encountered in OMCVD of ceramic compounds and moisture adsorbed at the surface of the initial granular precursor is a likely source of oxygen. The sources of oxygen in the deposits have been extensively discussed in a previous paper [8], and the very high reactivity of our chemical system at oxygen, act towards the reactor as an oxygen getter. The presence of H_2O or O_2 in the carrier gas that would result from small leaks at the reactor gaskets or contamination of the hydrogen carrier gas must be very low, as both hydrogen purity and reactor tightness were carefully checked. Moreover, the amount of oxygen in the initial granular precursor (vanadocene purity of 99.96%) is also low. Nevertheless, all these quantities are significant in a very reactive chemical system and can account for such an elevated amount of oxygen in the deposits.

According to both the elemental composition of the deposits (**table 2**) and V-C-O ternary phase diagram [17,18], the deposits should be two-phase materials: $\text{V}(\text{C},\text{O}) + \text{V}_2\text{O}_3$. Only the diffraction peaks corresponding to V_2O_3 were detected for the layers deposited from the sublimated precursor ($T_p = 393$ K). The lack of diffraction peaks corresponding to the $\text{V}(\text{C},\text{O})$ phase suggests that carbon is included in a non-crystallised phase. When the precursor is decomposed in the vaporization crucible ($T_p = 413$ K), neither V_2O_3 nor $\text{V}(\text{C},\text{O})$ phases were detected. However, all the coatings exhibited three diffraction peaks in the range 20 to $90^\circ 2\theta$. Though close to the peak positions characteristic of the steel substrate, these three peaks, which were also observed in the X-ray diffraction patterns obtained on a flake of deposit, are indeed characteristic of a crystallized phase in the deposit. As these peaks do not belong to any reference pattern of a known material in the V-C-O ternary phase diagram, the following structure is proposed. As a matter of fact, all the diffraction peaks can be indexed, assuming a cubic centered structure (**table 3**). A unit cell parameter of $0.35(1)$ nm was accordingly calculated.

(2 θ) diffraction peak (°)	d(hkl) (nm)	(hkl) for a cubic centered structure	Unit cell parameter (nm)
36.034	.249(0)	(110)	.352
64.960	.143(4)	(211)	.351
76.884	.123(9)	(220)	.350(5)

Table 3: characteristic (2 θ) diffraction peaks of deposits realised at 413 K. The unit cell parameter was calculated assuming a cubic centered structure.

4. CONCLUSION

These results put the emphasis on the influence of the vaporization temperature of the precursor on the properties of the materials deposited by OMCVD. In particular, it has been shown that the change of a sublimation vaporization procedure to a vaporization of the species resulting from the solid state decomposition of the precursor has a marked influence on both the deposition rate and surface morphology of the deposits. As expected, when the sublimated molecules of precursor were transported in the gas phase, the transport phenomena had almost no influence on the properties of the deposits, as the result of the lack of chemical reactivity of the gas mixture. In contrast, a more reactive gas mixture was obtained from the decomposition process, resulting in a strong influence of the hydrogen gas flow.

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References

- [1] I.I.Bilyk, *Poroshkovaya Metallurgiya* **114** (1972) 49.
- [2] A.A.Adamovskii, A.I.Bezykornov and I.I.Bilyk, *Poroshkovaya Metallurgiya* **136** (1974) 79.
- [3] L.Ramqvist, *Jernkontorets Ann.* **152** (1968) 517.
- [4] E.Horvath and A.J.Perry, *Thin Solid Films* **65** (1980) 309.
- [5] V.Norman and T.P.Whaley, PATENT N°3,175,924 DATE DEPOT: 30/05/65, PAYS: U.S.A.
- [6] G.M.Brown and L.Maya, *Inorg.Chem.* **28** (1989) 2007.
- [7] H.Berndt, A.Q.Zeng, H.R.Stock and P.Mayr, Proc. of the IX Euro. Conf. on CVD, Tempere Finland, Mäntylä T. (Ed), Colloque C3 Journal de Physique Supplément N°8, (1993) 313.
- [8] L.Poirier, O.Richard, M.Ducarroi, M.Nadal, F.Teyssandier, F.Laurent, O.Cyr-athis, R.Choukroun, L.Valade and P.Cassoux, *Thin Solid Films* **249** (1994) 62.
- [9] L.Valade, R.Choukroun, P.Cassoux, F.Teyssandier, L.Poirier, M.Ducarroi, R.Feurer, P.Bonnefond and F.Maury, In the press in 1995 International Chemical Congress of Pacific Basin Societies "Transition Metal Carbides and Nitrides: Preparation, Properties and Reactivity", December 17-22, Honolulu, Hawaii
- [10] L.Poirier, F.Teyssandier, F.Sibiode, R.Choukroun, L.Valade, and J.L.Jauberteau, "Thermal behavior of vanadocene", in preparation.
- [11] G.Wilkinson, F.A.Cotton and J.M.Birmingham, *J.Inorg.Nucl.Chem.* **2** (1956) 95.
- [12] C.Floriani and V.Mange, *Inorg.Synth.* **28** (1990) 263.
- [13] L.E.Manzer, *Inorg.Synth.* **21** (1982) 84.
- [14] G.E.P.Box, L.R.Connor, W.R.Cousins, O.L.Davies, F.R.Himsworth and G.P.Sillitto, O.L.Davies, (ed.), The design and analysis of industrial experiments, Oliver & Boyd, London, 1963.
- [15] R.PhanTan Luu, D.Feneuille and D.Mathieu, Méthodologie de la recherche expérimentale, IPSOI, Université, rue Henri Poincaré, 13397 Marseille Cedex France
- [16] N.R.Draper and H. Smith, Applied Regression Analysis, Wiley, New York, 1966.
- [17] K.Koyama, Y.Hashimoto and H.Hata, *Trans.Jpn.Inst.Met.* **20** (1979) 371.
- [18] L.Poirier, F.Teyssandier, "Thermodynamic approach of the OMCVD of vanadium oxi-carbide from vanadocene" in preparation.