TITANOCENE-DICHLORIDE AS A METALORGANIC SOURCE FOR TITANIUM CARBIDE

J. SLIFIRSKI*, G. HUCHET* and F. TEYSSANDIER**

* CNRS Institut de Science et de Génie des Matériaux et
Procédés, Université, avenue de Villeneuve,
F-66860 Perpignan cedex, France

** Etablissement Technique Central de l'Armement, 16 bis avenue
Prieur de la Côte d'Or, F-94114 Arceuil cedex, France

ABSTRACT The use of titanocene-dichloride (Cp_2TiCl_2) as a metalorganic precursor for TiC coating provides layers of very different quality according to its temperature of vaporization in a cold wall CVD reactor. The deposits observed by SEM and characterized by EPMA are related to the experimental procedure. The thermal behavior of the precursor investigated by thermogravimetry (TG), thermogravimetry coupled with differential thermal analysis (TG-DTA) and mass spectroscopy (MS) is used to determine the structural state of Cp_2TiCl_2 active from a CVD point of view.

INTRODUCTION

Due to its refractory nature ($\text{mp} = 3067^\circ\text{C}$), hardness, corrosion resistance, low friction behavior and high abrasion resistance, titanium carbide has been used as wear protective coating for many years. Initially deposited on cemented carbide cutting tools or inserts, its application field has considerably increased and a great variety of substrates are now industrially treated. In particular, many kind of steels are coated to provide interesting surface properties.

The initial gas mixture of the industrial process is composed of hydrogen, methane and titanium tetrachloride. The high temperatures ($T > 950^\circ\text{C}$) required to obtain satisfactory deposition rates are responsible for many drawbacks such as: residual stresses, grain growth of the substrate structure, stabilization of the austenite structure in the case of steel substrates, decarburization of carbon-containing substrates and, more generally, solid state modifications or interactions with the substrate.

In order to overcome these problems, it is worth lowering the process temperature, which can be achieved by the use of less stable precursors such as metalorganic compounds.

PREVIOUS WORK ON MOCVD OF TITANIUM BASED COMPOUNDS.

Deposits generally carried out at temperature below 500°C lead to amorphous titanium-based materials even if X-ray diffraction reveals the presence of very small crystals for specific experimental parameters. Metalorganic chemical vapor deposition of titanium rich deposits ($\text{Ti}(\text{C},\text{N},\text{H})$) were obtained by Morancho and al. [1-2] in the temperature range $370\text{--}520^\circ\text{C}$ from $\text{Tris}-(2,2'\text{-bipyridine})$. Tetraneopentyltitanium ($\text{Ti}[\text{CH}_2\text{C}(\text{CH}_3)_3]_4$) has also been used successfully in a slightly lower temperature range ($150\text{--}300^\circ\text{C}$) [3-4] to deposit ($\text{Ti},\text{C},\text{H}$) materials. In both cases, pressures are below 10^{-5} torr. More recently [5], amorphous (300°C) and crystalline ($400\text{--}580^\circ\text{C}$)

TiN have been deposited under 0.3 Torr from an initial mixture of tetradimethylamino-titanium ($\text{Ti}(\text{N}(\text{CH}_3)_2)_4$) and NH_3 .

In all cases very low deposition rates are observed (lower than $0.4 \mu\text{m/h}$). Furthermore, these metalorganic compounds are very sensitive to oxygen and moisture and great care must be taken to avoid pollution.

EXPERIMENTS

Experiments were carried out in a classical cold wall reactor. The polished steel substrate is heated by an r.f coil. Its temperature is adjusted by a chromel-alumel thermocouple inserted in a hole drilled in the back face. The crucible is heated by a resistor wrapped around it and equipped with a thermocouple. In order to prevent extra heating of the metalorganic compound by radiation from the substrate, the receiving crucible is covered by a lid with a hole drilled in the middle (diam. = 1 mm). The carrier gas flowrate (hydrogen) is controlled by means of a mass flowmeter and the distance between the crucible and the substrate is 40 mm.

The following experimental procedure is used. The substrate is first heated to the deposition temperature under hydrogen flow, then two ramps of temperature are successively applied to the receiving crucible: $10^\circ/\text{min}$ from 25°C to 200°C and $1^\circ/\text{min}$ from 200°C to the terminal temperature which is held for 5 hours. When the substrate temperature and the terminal temperature of the crucible are respectively $T_s=750^\circ\text{C}$ and $T_p=400^\circ\text{C}$ the deposit observed on a polished cross-section presents two layers of different thickness as shown in **figure 1** [6]. The layer adjacent to the substrate is $6 \mu\text{m}$ thick and composed of many sublayers with a mean thickness lower than $0.5 \mu\text{m}$. The second one is thicker ($e=10 \mu\text{m}$) and homogeneous in composition. Both layers present a high carbon content (near 60 at%) as measured by EPMA, due to an initial molecule including two Cp groups. But the main difference concerns the oxygen and chlorine amounts. The first layer includes almost no chlorine but the oxygen content, depending on the sample, ranges between 10 and 20 at%. The oxygen concentration in the homogeneous layer does not exceed 2 at% and the chlorine content is about 1 at%. Two typical compositions are given as an indication: 1) $\text{Ti}_{0.34}\text{C}_{0.57}\text{O}_{0.09}$ 2) $\text{Ti}_{0.38}\text{C}_{0.59}\text{O}_{0.02}\text{Cl}_{0.01}$. The composition of layer 1 is calculated as a percentage, though the total of the mass fractions obtained after the ZAF corrections is significantly lower than one in every case. This phenomenon probably results from the inhomogeneities of the layer as observed by SEM.

The same experiment carried out at $T_p=280^\circ\text{C}$ provides only a very thin layer ($\approx 1 \mu\text{m}$) which has not been analysed.

A modification of the experimental procedure allows the suppression of the layer composed of many sublayers. The crucible is heated to 300°C with the two ramps already mentioned but the temperature of the substrate is maintained during this process at a low temperature (250°C) which inhibits surface reactions and prevents condensation of the metalorganic compound. Then the substrate temperature is raised to 750°C for 5 hours. Only the type 2 layer is obtained with a thickness of $15 \mu\text{m}$ **figure 2**. It is worth mentioning that such a thickness is perhaps reached in less than 5 hours. As a matter of fact previous experiments [6] have shown that a $7 \mu\text{m}$ thick layer can be deposited within 50 min at 700°C , which corresponds to a deposition rate higher than $8 \mu\text{m/h}$.

FIGURE 1: Two types of TiC layer.

FIGURE 2: 15 μm homogeneous TiC layer.

These experiments show the influence of the vaporization temperature of Cp_2TiCl_2 . We will now try to understand the structural modifications thermally induced in the metalorganic precursor that are responsible for these various type of coatings.

THERMAL ANALYSIS

The thermal behavior of Cp_2TiCl_2 was first investigated with thermogravimetry (T.G) and then with thermogravimetry coupled with differential thermal analysis (DTA)

THERMOGRAVIMETRY (Perkin Elmer TGS2)

Cp_2TiCl_2 was heated at different rates from 5 to 20 $^\circ\text{C}/\text{min}$ under a nitrogen flow. The curve presented in **figure 3** obtained at 15 $^\circ\text{C}/\text{min}$ is typical of the thermal behavior of the compound and shows four main domains :

- up to 190 $^\circ\text{C}$ no weight loss is observed,
- from 190 $^\circ\text{C}$ to 310 $^\circ\text{C}$, 60 weight % of the product is lost at a fast rate,
- from 310 $^\circ\text{C}$ to 680 $^\circ\text{C}$, about 24 weight % is lost,
- above 680 $^\circ\text{C}$ no appreciable modification can be detected.

FIGURE 3: Thermogravimetry of Cp_2TiCl_2 with a temperature ramp of 15 $^\circ\text{C}/\text{min}$.

The total weight loss of the sample is 84 %. From this curve two main phenomena are observed. The derivative signal which indicates the maximum speed for each phenomenon presents two minima at 280 and 350 °C. Due to thermal and mass transfer in the crucible the temperature corresponding to these maxima are function of the applied ramp: higher rates shift the peaks towards high temperatures.

These values recorded for different ramps are plotted in **figure 4** and allow the extrapolation of the temperatures corresponding to the static transformation: 258 °C and 290°C.

FIGURE 4: Variation of the temperature corresponding to the maximum rate of the three transformations observed for Cp_2TiCl_2 and plotted as a function of the ramp.

290 °C is the established melting point from the literature but 258 °C does not correspond to any physical phenomenon known about Cp_2TiCl_2 . In order to confirm these results experiments were undertaken in a TG-DTA device.

THERMOGRAVIMETRY coupled with DIFFERENTIAL THERMAL ANALYSIS.(Setaram DT-TGA92)

The metalorganic compound is disposed in an alumina crucible hanging from the beam of a micro-balance and located in the middle of a vertical furnace. An identical crucible filled with a non-reactive compound is heated together. The heat flow is monitored with thermocouples which equip both crucibles. The device was used either with nitrogen or hydrogen but the nature of the gas had no significant influence on the spectra. The heating rate was set at the lowest available value: 1°/min. The mass loss and the heat flow recorded from 200 to 300°C are presented in **figure 5**.

The differential thermogravimetric signal presents two main peaks at 270 and 285°C. (We must also mention the additional peak at 291 °C which is reproducible and therefore seems to be meaningful). Two endothermic peaks are observed at the same temperatures. These values plotted in **figure 3** are in good agreement with the previous TG measurements and we may reasonably assume from these measurements that the second event is the melting of Cp_2TiCl_2 .

FIGURE 5: Comparison between the heat flow and the differential thermogravimetric signal of Cp_2TiCl_2 heated at a rate of $1^\circ/\text{min}$ from 200 to 300°C .

Additional experiments were performed to determine the thermal behavior of the metalorganic compound under isothermal conditions. The mass loss is then recorded as a function of time at a constant temperature which is imposed very rapidly ($120^\circ/\text{min}$) without any overshoot. The mass fraction of the residue is plotted in **figure 6** against the level temperature.

FIGURE 6: Residual mass percentage as a function of the temperature of the isothermal treatment.

The results obtained below 200°C are not plotted because the sample was still losing mass after 8 hours, which was the duration devoted to the experiment. The increasing mass fraction of the residue from ≈ 190 to 300°C is a proof of the transformation of Cp_2TiCl_2 below the melting point. The elemental composition of the remaining product at temperatures below 290°C , determined by chemical analysis give the same composition as the starting compound. A decomposition would have formed by-products of different volatility providing a composition of the residue different from Cp_2TiCl_2 . We may then consider that a dimerization or a polymerization is the most

probable type of transformation occurring between 190 and 290 °C. The slight variation of the molecular formula involved in the dimerization of such compounds remains within the uncertainty of the chemical analysis.

Above 300° C the residual mass fraction decreases, which is an indication of a decomposition process. The morphology of the residue depends very much on temperature: from 50 to 280°C it has the same appearance as the initial product which is red and well crystallized. When maintained at 280°C it turns progressively to black but still presents the same crystalline structure. Residues from Cp_2TiCl_2 heated above 300 °C look like solidified tar and are no longer soluble in toluene. The decomposition of Cp_2TiCl_2 above 300°C is confirmed by mass spectroscopy measurements.

MASS SPECTROSCOPY

Neutral species resulting from the vaporization and/or decomposition of Cp_2TiCl_2 are studied by means of a Finnigan Mat 8002 quadrupole spectrometer. The compound is introduced directly into the ionization chamber of the apparatus. Electron impact spectra using 70 eV electrons were recorded at different temperatures of Cp_2TiCl_2 heated in situ at a rate of 12 °/min. Two different spectra are observed. Below a transition temperature which is estimated at 310 °C the monomer (m/e 248) and fragments resulting from electron impact are mainly observed. Above that transition temperature the importance of the low m/e fragments increases rapidly and the occurrence of HCl (m/e 36) reveals the decomposition of the molecule.

Mass spectrum of Cp_2TiCl_2 FIGURE 7: below 310°C FIGURE 8: above 310°C

CONCLUSION

All these measurements provide a coherent set of information on the thermal behavior of Cp_2TiCl_2 . It sublimates without any structural modification up to 190 °C. In the temperature range 190-290 °C the sublimation is in competition with a phenomenon which increases the amount of the residue but does not fundamentally change the elemental composition. This structural modification is supposed to be a dimerization (or a polymerization). 290 °C may be the melting temperature of the monomer or the dimer as stated in the literature but this physical transformation is accompanied or immediately followed by a decomposition of the compound. This decomposition, which is kinetically controlled though the melting is only limited by heat transfer (in the absence of metastable equilibria), can account for the rather high slope of

transformation 2 observed as a function of the heating rate in **figure 4**. From a CVD point of view the sublimation of the molecule and its subsequent decomposition in the thermal gradient layer in the vicinity of the substrate or the transfer in the gas phase of by-products (and probably also their transformation in the thermal gradient layer) resulting from the decomposition in the crucible are not at all equivalent. In the first case a coating of poor quality is obtained at a low deposition rate though the preliminary thermal decomposition provides at a higher growth rate a good quality layer.

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REFERENCES

- /1/ Morancho R. , Constant G. , Ehrhardt J.J. ,
Thin solid film, 77 (1981) 155.
- /2/ Morancho R. , Petit J.A. , Dabosi F. , Constant G.,
J. Electrochem.Soc., 129,4 (1982) 854.
- /3/ Kaloyeros A.E. , Hoffman M.P. , Williams W.S. ,
Thin Solid Films, 141 (1986) 237.
- /4/ Girolami G.S. , Jensen J.A. , Pollina D.M., Williams W.S. , Kaloyeros A.E. ,
Allocca C.M. ,
J. Am. Chem. Soc., 109 (1987) 1579.
- /5/ Ishihara K., Yamazaki K., Hamada H., Kamisako K., Tarui Y.,
Jpn.J.Appl.Phys., 29,10 (1990) 2103.
- /6/ Huchet G., Teyssandier F.,
Proc. of the XI Intern. Conf. on CVD, Cullen G.W. , Spear K.E. (Eds),
Seattle USA, (1990) 703.