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CHARACTERIZATION OF SINTERED HARDMETALS COATED WITH TiC

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ABSTRACT

This paper presents the realization of TiC thin films by CVD method. The thin layers of TiC thicknesses were 8 and 10µm, their thickness increasing with time, keeping the temperature. Diffractometer analysis certifies that this thin layer of TiC is homogeneous and unscratched. Microhardness of thin layers of TiC is $HV_{0,05}$ = 30000MPa compared to WC (carbide substrate of the component) that has a microhardness $HV_{0,05}$ = 17000MPa.

KEYWORDS: method, diffractometer analysis, microhardness

1. Introduction

Mono-based sintered hardmetals, WC-Co, are mainly used for cutting materials and parts for wear resistant applications.

Chemical Vapor Deposition is a widespread method of forming thin layers. In today's world, it is estimated that 30-40% of all exchangeable cutting plates, sold, are covered by CVD method [1].

Technology of thin films of titanium carbide wear resistant vapor phase followed an original way of achieving titanium tetrachloride directly inside the heat treatment, thus avoiding the import of these tetrachlorides which present a high toxicity. For the ferrotitanium technology with positive results we obtained using ferroalloys with higher concentration of 65% titanium. Ferrotitanium technology shows economic interest as it eliminates the drawbacks of tetrachloride which is highly corrosive titanium and us instead ferrotitanium.

2. Experiments

Titanium tetrachloride vapor is obtained directly in the deposition reactor, the reaction of hydrochloric acid vapors passed over incandescent ferrotitanium (1120^{0}C).

Installation of obtaining thin layers of TiC, (Figure 1), includes the following main parts: 1 - sources of Gas; 2- flowmeters; 3 – evaporator; 4- the working chamber; 5, 6 - air purification; 7 - widia plates; 8 - neutralization vessel.

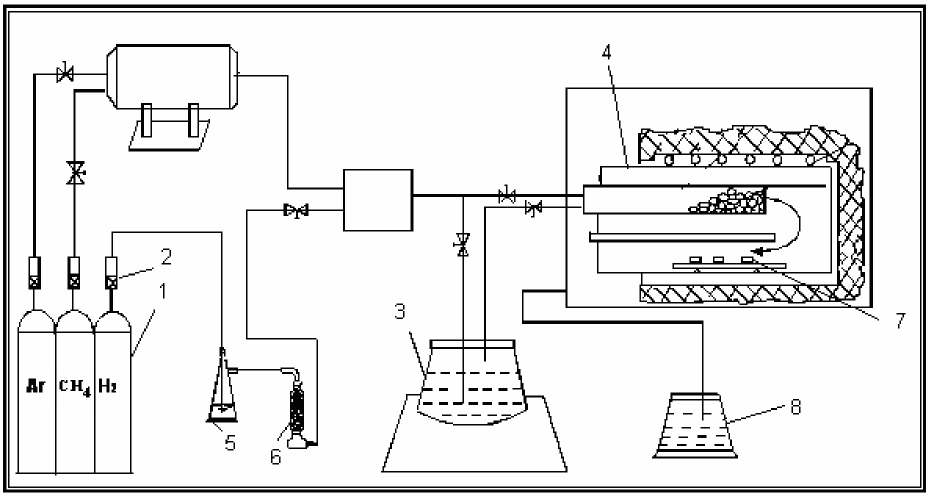


Fig. 1. *Installation of obtaining thin layers of TiC*

In developing the system layer deposition technology, it occurs the simultaneous deposition on the entire the working chamber, a particular temperature profile combined with a time ratio of the volume of gas in the mixture. This is achieved with a thermocouple and pressure flow meters [2].

Titanium tetrachloride is obtained from rutile, ilmenite, titanium slag, titanium oxide and methane gas according to the reaction:

$$TiO_2 + C + 2Cl_2 \Leftrightarrow TiCl_4 + CO_2 + 56kcal/mol$$

$$2TiO_2 + 2C + 4Cl_2 \Leftrightarrow 2TiCl_4 + 2CO_2 + 11kcal/mol$$

Reactions being endothermic, require heat entering the system. In this work, titanium tetrachloride is obtained directly in the working chamber of the ferrotitanium and concentrated hydrochloric acid at elevated temperature (over 1000^{o}C) according to the reaction:

$$Ti_{(s)} + 4HCl \rightarrow TiCl_4 + 2H_2$$

$$TiCl_4 + CH_4 + H_2 \rightarrow TiCl + 4HCl + H_2$$

Figure 2 shows the equilibrium diagram Ti-C.

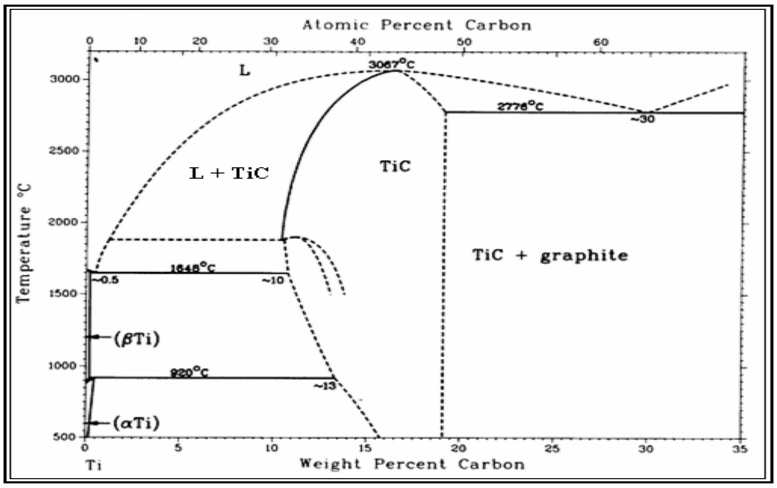


***Fig. 2**. Diagram of equilibrium Ti-C system, [3]*

We can make the following considerations:

- diagram contains narrow areas of solubility of carbon in αTi and βTi;
- titanium carbide (TiC) has a wide range of homogeneity;
- the lower border of the solubility of carbon in TiC eutectic temperature Ti – TiC (1645 ºC) [3].

In Table 1 are presented the main characteristics of titanium carbide [4].

***Table 1**. Properties of TiC carbide*

Property	u.a.	TiC
Report ray C/Ti		0.52
Carbon content	%	20.05
Temperature homogeneity range 1750°C	%	11-20
Type and lattice parameters	Å	Cubic a=4.317 Å
Density	g/cm^3	4.92
Enthalpy of formation of elements ΔH0298	Kcal/mol	-55.3
Standard entropy S0298	Kcal/mol	5.8
Entropy training elements Δ S0298	Kcal/mol	-2.92
Specific heat 298..2073 °C	Kcal/mol	$11.83{+}0.8\cdot10^{-3}T-3.58\cdot10^{-5}T-2$
Melting point	°C	3257
The evaporation temperature	°C	4300
Tensile resistance	MPa	0.65
Flexural	MPa	0.15
Compressive strength	MPa	13.8
Modulus of elasticity	MPa	4600
Mineralogical hardness scale	-	8-9
Rockwel Hardness HRA	MPa	9.25- 9.35
Microhardness H_{μ}	MPa	317±17

Uncoated (TPUN22.04.08 type P30 and SNUN15.04.08 type K20) and coated plates of TiC were tested, Figure 3. Microstructure of samples analyzed indicate that they belong to the user group P (WC-Co-TiC) and revealed the presence phases α, β and no η phase [5, 6].

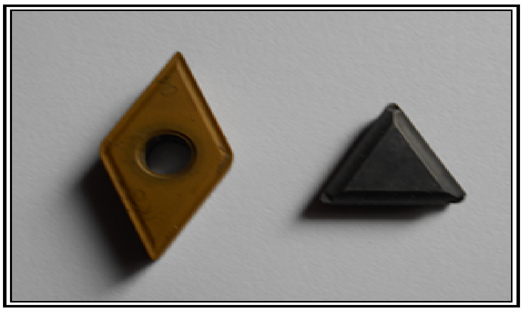
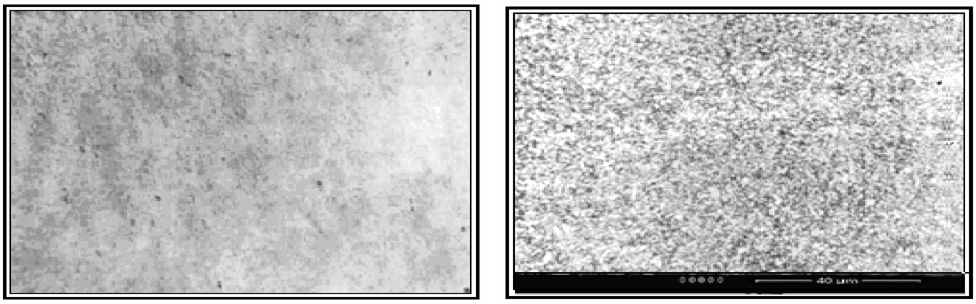


Fig. 3. *The visual appearance of widia plates-type P30 and K20*

Figure 4 shows the SEM micrography: a- structure unassailable of alloy with 5% Co and 95% WC and b- structure attacked of alloy with 5% Co and 95% WC. This structure represents the type of structure characterized by the predominance of non-crystallising tungsten carbide with very fine grains. This type of tungsten carbide is called α - metastable constituent, whose size grading upward transformation is inevitable during sintering.



a) b)

Fig. 4. *SEM micrography: a - unassailable, b - attacked of alloy with 5% Co and 95% WC, X500*

Figure 5 presents the microscopic appearance of the sample in the interface coating-substrate separation and SEM micrograph of TiC surface layer is presented in Figure 6.

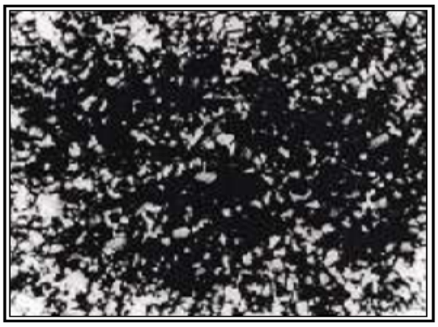


Fig. 5. *SEM micrograph in the interface coating-substrate separation (attack Murakami, x 2000)*

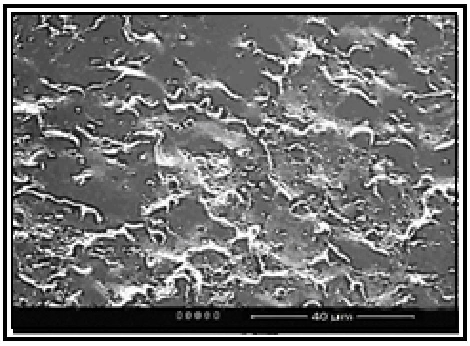
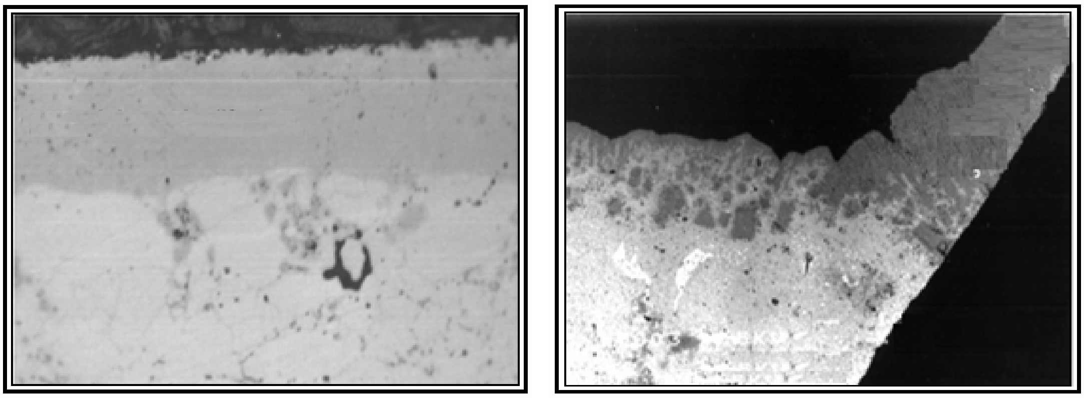


Fig. 6. *SEM micrograph of TiC, x2000*

In Figure 7a is shown thin layer of TiC of 10 μm, thickness layer is uniform, homogeneous and adherent throughout its depth and in Figure 7b is presented a diffusion layer by dispersion X ray camera.



a) b)

Fig. 7. *a) SEM micrograph of the TiC layer with a thickness of 10μm; b) Diffusion layer by retrodispersie ray camera, X 2000*

Diffractometer analysis was performed by X-ray diffraction (XRD) on plates coated with thin layers of TiC to working temperature 1120°C. Diffractogram was obtained with a diffractometer equipped with a horizontal goniometer (Figure 8) [7].

XRD spectra were recorded at room temperature and diffractometer using CoKα radiation (λ=1,79 A°) in 2θ configuration ranged between 40° and 70°, at 40 kV tension and 30mA current intensity with a scanning speed of 0.02°/min and acquisition time of 1s/step.

The specific lines are tall and narrow, (111) plane corresponds to the angle 2θ = 16.5°, (220) plane corresponds to the angle 2θ = 21.73°, and (200) plane corresponds to 2θ = 20.25°. The result is favorable evidences TiC layer (the highs curves diffractometer).

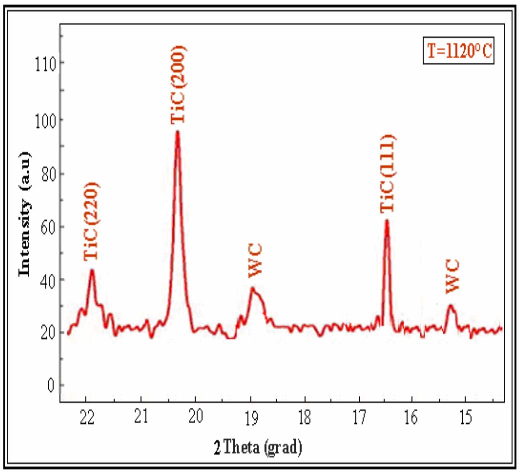
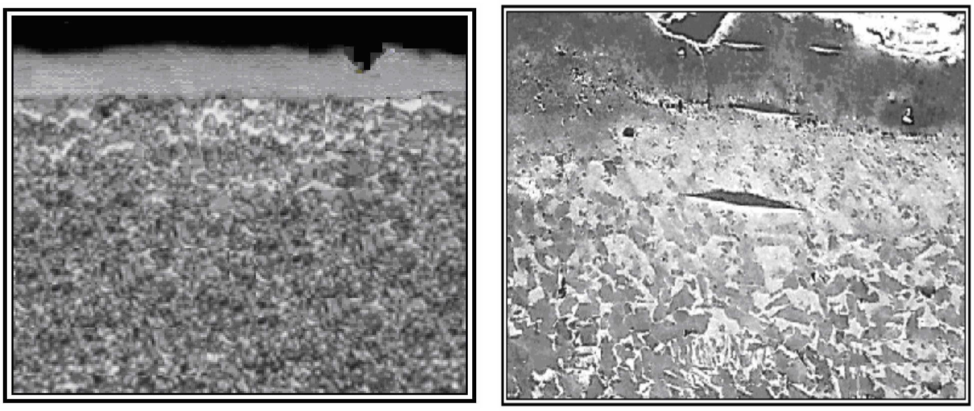


Fig. 8. *XRD analysis for the thin layer of TiC*



a) magnification x1000 b) magnification x 2000

Fig. 9*. Microhardness deposited layer of TiC - cross section*

The results are in agreement with the literature [8, 9].

Layers Microhardness Vickers method was performed by using an optical microscope type M-400-H1 (Hardness Testing Machine) [10]. The microhardness determinations were carried out on plates coated with thin layers of TiC with thickness of 10μm.

Microhardness Vickers is not a constant as Vickers hardness, with all geometric similarity of fingerprints, but generally decreases with increasing test load. [11].

Figure 9 a, b presents microhardness TiC coated plates in cross section at different magnifications and in Figure 10 are presented $HV_{0.05}$ microhardness prints in the substrate. The microhardness tests show a hardness value of $HV_{0.05}$ = 30000 MPa coated with TiC layer, a value that is consistent with data from the literature in relation to the microhardness substrate (95% WC - 5% Co) which is $HV_{0,05}$ = 17000 MPa.

In terms of hardness, there is a strong correlation between Co and hardness of WC-Co alloys, the hardness decreases with increasing cobalt content [12].

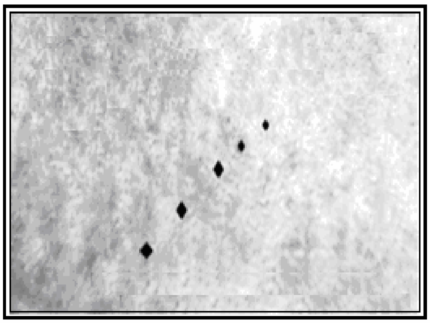


Fig. 10. *Prints of microhardness $HV_{0,05}$ in the substrate (magnification x 1000)*

3. Conclusions

- Titanium carbide thin layers obtained by chemical vapor deposition method, followed a realization original titanium tetrachloride directly in the working chamber, thus avoiding import this tetrachloride showing a high toxicity.
- Titanium tetrachloride is given directly the thermal treatment chamber by the use of hydrochloric acid vapors passed over the incandescent ferrotitanium (or pure titanium).
- It was established a substrate temperature of ~ 1120^{o}C at which TiC can be achieved.
- SEM micrographs have a suitable structure.
- Thickness layer is uniform, homogeneous and adherent throughout its depth.
- The diffractometer analysis is favorable evidences TiC layer.
- The microhardness tests show a hardness value of $HV_{0,05}$ = 30000 MPa coated with TiC layer.

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