THE ANNALS OF "DUNAREA DE JOS" UNIVERSITY OF GALATI
FASCICLE IX. METALLURGY AND MATERIALS SCIENCE
Nº. 3 - 2015, ISSN 1453 – 083X

THE PROTECTIVE BEHAVIOUR OF TITANIUM NITRIDE COATINGS

Stela CONSTANTINESCU
"Dunarea de Jos" University of Galati, Romania
e-mail: constantinescu_stela@yahoo.com

ABSTRACT

The experiments conducted to obtain a thin layer of nitride through the vapour chemical deposition method have followed an original path to obtain TiN directly in the working room thus avoiding the import of these hazardous substances. In this paper, the protective behaviour of titanium nitride coatings onto hard carbide substrate was investigated using scanning electron microscope (SEM), X-ray diffractometer (XRD) and Knoop hardness. Scanning Electron Microscope was used to investigate the coating morphology and interface structure. X-ray mapping was also performed to characterize the elements in a semi-quantitative analysis. Dron X-ray diffractometer with Mo K_α radiation operating was used for phase(s) identification. Microhardness value (Knoop hardness) measured in the coating layer was 28.000 MPa. CVD TiN coatings usually show only moderate or even poor corrosion protection for hard carbide substrates.

KEYWORDS: thin layer, titanium nitride, protective coatings, corrosion, microhardness

1. Introduction

Titanium nitride coatings find extensive applications in tribilogical, mechanical and even decorative applications. CVD TiN coatings usually show only moderate or even poor corrosion protection for hard carbide substrates. The poor corrosion performance is not due to the intrinsic corrosion behaviour of the nitride coating itself. It results from small structural defects, pores and crack formed during or after deposition, which act as channels for the corrosion of the substrate. We investigated the corrosion tests in water of titanium nitride coatings elaborated by the CVD process.

If the vapour chemical deposition takes place within a tubular continuous reactor, a gas carrying the reacting species is passed over the sub-layer. At the sub-layer surface, the reacting elements undergo a number of chemical reactions leading to product formation. Part of the products are deposited on the sub-layer and part of it goes back to the gas stream [1, 2].

Before examining the vapour chemical deposition reactions, it must be determined if the reaction is possible thermodynamically. The reaction will be possible thermodynamically if the calculated concentrations (partial pressures) of the reactants, under equilibrium conditions, are less than their original concentrations.

The calculation of the equilibrium concentrations from the equilibrium constant involves a good choice of the number of gas spaces which can be higher than two and the number of independent relations. A relation implies the equilibrium expression depending on the free standard reaction energy and temperature.

The other relation consists in that the system pressure is the sum of the partial pressures. If some reactants possess more than one valence state, the reaction should contain the reactant under its most stable valence state [3, 4].

During the corrosion test in water, samples covered with TiN channel are stronger compared to uncoated samples TiN [5, 6].

Hard alloys made out of metallic carbides manufactured at an industrial scale for cutting processing can be divided into two categories, to investigate the coating morphology and interface structure. X-ray mapping was also performed to characterize the elements in a semi-quantitative analysis. Dron X-ray diffractometer with Mo K_α radiation operating was used for phase(s) identification. The microhardness tests show that we have TiN, value $HV_{0,05}$ = 28 000 MPa is in good agreement with the data from the literature.

2. Characterization

The characterization of the coating deposed by CVD method was done using scanning electron microscope (SEM), X-ray diffractometer (XRD). The TiN coated plates feature higher endurance capabilities than those uncoated for the same cutting speed both for steel and white cast iron.

The parameters of the cutting conditions were chosen in the range of the values used on the working machines at Arcelor Mittal Steel Galati.

Table 1. *Domains of the parameters values of the cutting conditions*

Plate type	Processed material	n [rot/min]	v [mm/min]	s [mm/rot]	t [mm]
SNUN 15.04.08 K20	white cast iron	450	110	0,096	0,5
		500	123	0,096	0,5
		530	130	0,096	0,5
		570	140	0,096	0,5
		610	150	0.096	0,5
		630	154	0,096	0,5

In Table 1 the values of the parameters of the cutting conditions are shown, where: n: rotation speed [rot/min]; v: speed cutting [mm/min]; s: advance [mm/rot]; t: deep cut [mm].

The operation of the latter is based on a housing which cuts the deposited TiN layer. Samples for metallography were prepared by polishing, this prevented damage to the dissimilar interface (strate – substrate) during polishing. SEM was also used.

3. Results and discussion

The optimum layers in the cutting process are the TiN layers. Having thickness within 4-10 μm above these values, the layers lose tenacity and become fragile. As a result of the thermal treatment which means heating up to 1050 ºC degrees for various exposure times, layer thickness within 3.5-10 μm was achieved [7]. The thickness of the thin layers increases with the time of exposure to the working temperature as illustrated in Fig. 1.

The micro-hardness of WC-TiC-Co alloys is affected by a large number of elements connected to the raw material, purity and component dispersion in the alloy and the solid solution quality and grain size of components.

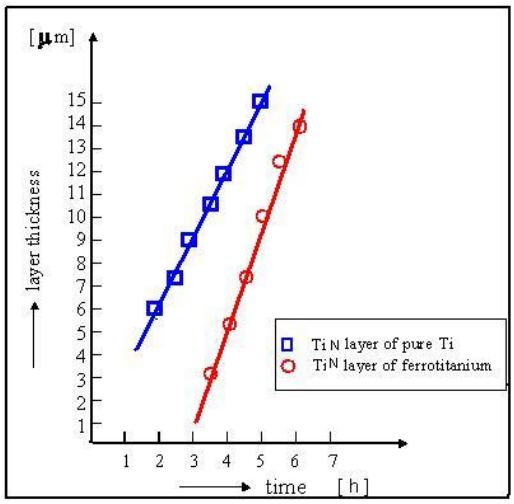


Fig. 1. *The thickness of the thin TiN layers increases with time*

In the factory process, these elements are playing an ultimate role in effective micro-hardness measurement of the material with a given chemical composition (Fig. 2).

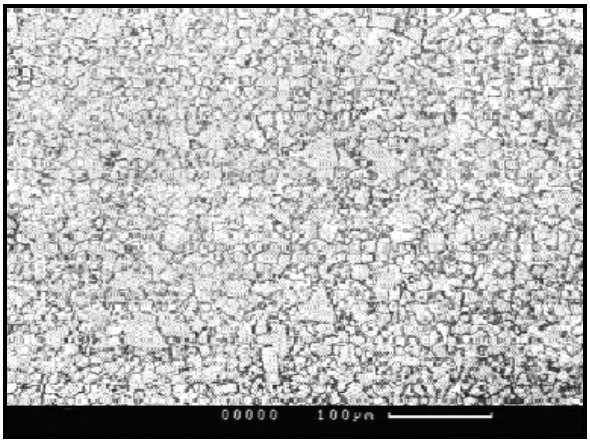


Fig. 2. *Metallographic appearance of alloy with 82%WC, 12%TiC, 6%Co, x1500*

Micro-hardness is not a constant like Vickers hardness, in spite of the geometrical similarity, but decreases with higher testing charges depending on the size of the print.

Measurements were made on TiN covered thin plates whose thickness ranges between 6, 8 and 10 μm [8, 9].

Micrography, Fig. 3-5, shows an adherent layer which is uniform and homogenous over the entire depth [10].

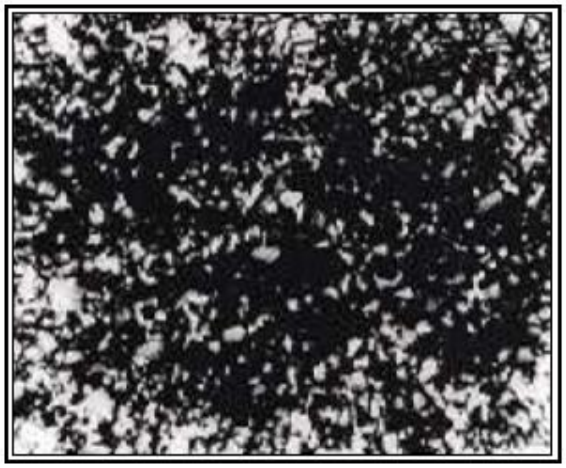


Fig. 3. *Uncoated plate surface appearance - SEM electron microscopy*

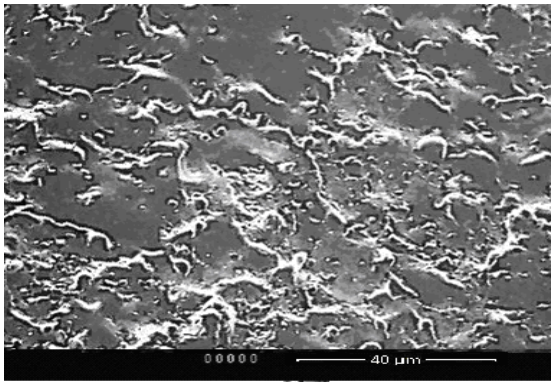


Fig. 4. *SEM image of a monolayer covered surface plate, appearance TiN*

Figures 3 and 4 show the superficial aspects of the CVD deposited layers, compared to TiN monolayer uncovering a plate, classic appearance, studied by electron microscopy. It is a clear difference in crystals, in layer size, uniformity and surface roughness [11].

In Figure 5 metallographic appearance is set for good quality coated plates. TiN coating has uniform thickness and the grain has a crystal columnar layer.

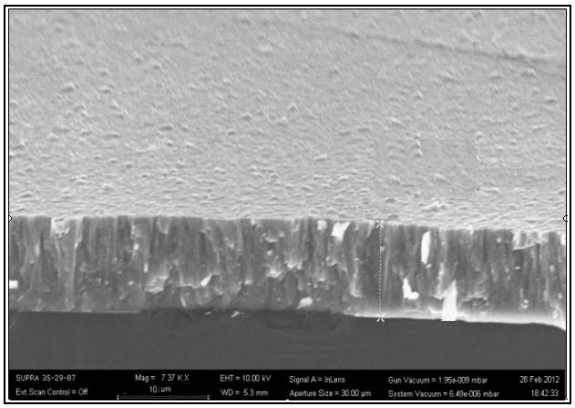


Fig. 5. *SEM images of TiN layer*

The almost uniform grain isomorphic layer and its purity ensure proper behavior at cutting premises. The best results are obtained for layer depth of 8 µm, with homogeneous and even structure, a feature that can be emphasized by means of diffraction pattern analysis, Fig. 6.

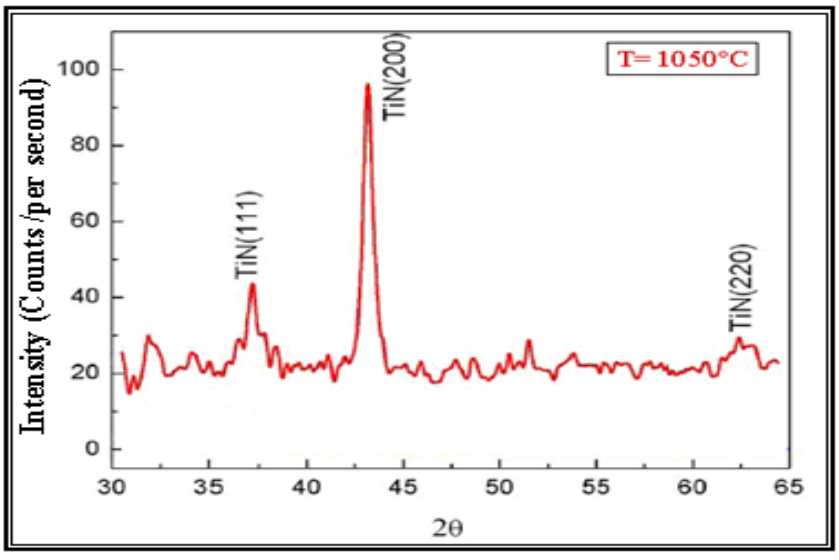


Fig. 6. *X- ray diffraction spectrum of TiN coating*

The titanium nitride coating diagram (Figure 6) presents diffraction lines which are characteristic to the most intense peak of TiN compound and correspond to the (200) diffraction plane [12]. The values of the thin TiN layers as measured by the Kalotest (Fig. 7) device are in good agreement with the values measured by microscopic analysis but slightly lower.

The steel ball diameter is 12 mm. Therefore, the shell diameter is much less than that of the ball.

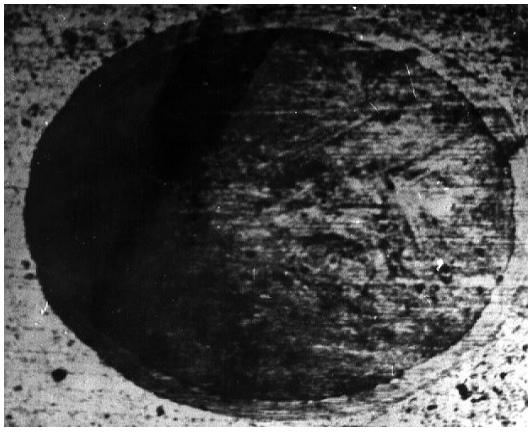
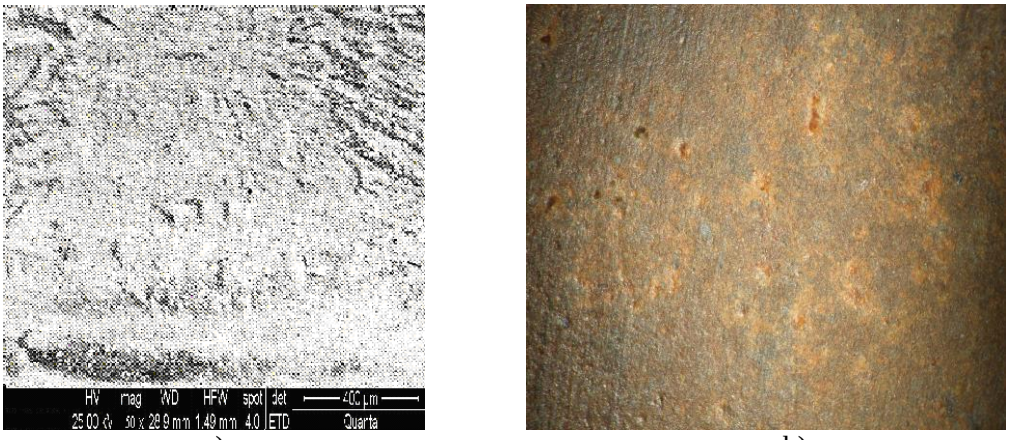
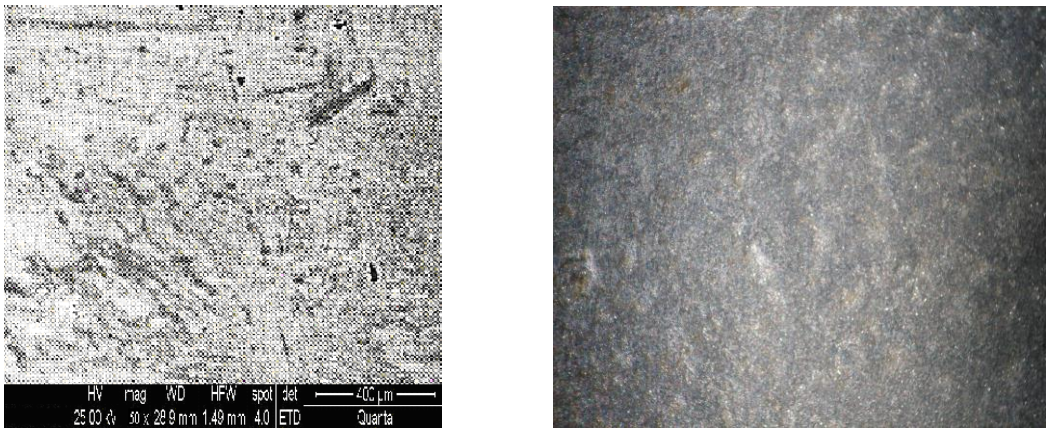


Fig. 7. *The sphere shell of TiN by the Kalotest*



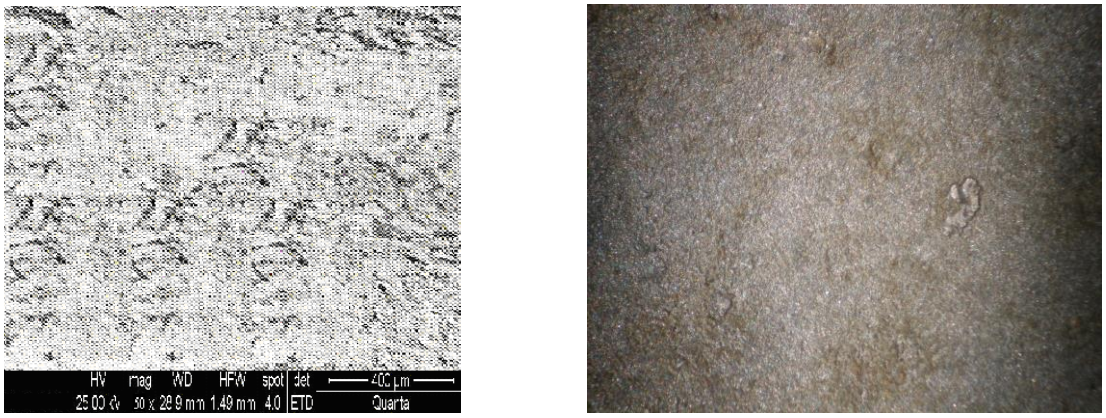
a) b)

Fig. 8. *Surface appearance of uncoated TiN samples: a) before corrosion, b) after corrosion*



a) b)

Fig. 9. *Surface appearance of covered TiN samples 6 µm: a) before corrosion, b) after corrosion*



a) b)

Fig. 10. *Surface appearance of covered TiN samples of 8 µm: a) before corrosion, b) after corrosion*

As seen in Figures 8-10, uncoated surface TiN samples have surface oxides by 70% if the samples coated with the thickness of 6 µm TiN have slight traces of surface oxides on 5% non-stick surface, and covered with TiN samples with thickness of 8 µm the surface shows no oxides. It is noted that in corrosion test in water samples covered with TiN, channel is stronger compared with uncoated TiN samples [13].

4. Conclusions

These coatings have good wear resistance, abrasion resistance, corrosion resistance and a strong strate-substrate interface. This leads to formation of thick and rough coating. The coating is fine grained, adherent, dense and free from cracks. However, some porosity is observed in the coating layer.

The widia plates coating with thin TiN layers entirely suppresses the inconveniences of a relatively rough topography of the common sintered nitrides while preserving the adequate material mechanical strength.

The layer begins losing its tenacity if its thickness increases considerably, exceeding the thickness of 10 µm mainly due to the lower strength characteristics. This together with the increase in the inner tensions results in cracks and breakings in the layers. This has been attributed to poor wetting characteristics.

During the corrosion test in water, samples covered with TiN channel are stronger compared to uncoated TiN samples.

Reference

[1]. S. Constantinescu, *Studies on Thin Carbide and Nitride Layers Deposition on Metal Basis, Based on Chemical Reaction at High Temperatures*, Academic Thesis, Galati, 1998.
[2]. S. Constantinescu, *Nitride coatings on widia substrate for mechanical applications*, Journal Surface Engineering, vol. 1, p. 77-81, 2009.
[3]. S. Constantinescu, T. Radu, *Advanced methods of obtaining thin coats*, Ed. Științifică F.M.R. ISBN 973-8151-25-2, București, 2003.
[4]. I. M. Notter, D. R. Gabe, *Porosity of Electrodeposited Coatings: Its Cause, Nature, Effect and Management*, Corrosion Reviews, 10 (3-4), p. 217-280, 1992.
[5]. J. Munemasa, T. Kumakiri, *Effect of the Surface Roughness of Substrate on the corrosion properties of fims coated by Physical Vapour Deposition*, Surface and Coatings Technology, 49, p. 496-499, 1991.
[6]. L. Orac, V. Grechanyuc, *Corrosion resistance of the composites Cu-Mo obtained by PVD method*, METAL 2010, Ostrava, Czech Republic, p. 932-937, 2010.
[7]. A. Zhecheva ,W. Sha, S. Malinov, A. Long, *Enhancing the microstructure and properties of titanium alloys through nitriding and other surface engineering methods*, Surface and Coatings Technology, vol. 200, issue 7, p. 2192–2207, 2005.
[8]. K. L. Choy, *Chemical vapour deposition of coatings*, Progress in Materials Science, 48, p. 57–170, 2003.
[9]. E. Bemporad , M. Sebastiani, C. Pecchio , S. De Rossi, *High thickness Ti/TiN multilayer thin coatings for wear resistant applications*, Surface and Coatings Technology, vol. 201, issue 6, p. 2155-2165, 2006.
[10]. J. C. Caicedo, C. Amaya, L. Yate, O. Nos, M. E. Gomez, P. Prieto, *Hard coating performance enhancement by using [Ti/TiN]n, [Zr/ZrN]n and [TiN/ZrN]n multilayer system*, Mater. Sci. Eng. B, vol. 171, p. 56-61, 2010.
[11]. O. Yasuharu, K. Shinya, O. Kazuhide, A. Hideki, N. Hideki, H. Kenji, M. Osamu, Thin Solid Films, 497, 2006.
[12]. A. D. Krawitz- *Introduction to Diffraction in Materials Science and Engineering*, Wiley, New York, p. 165-167, 2001.
[13]. V. Sista, O. Kahvecioglu, O. L. Erylmaz, A. Erdemir, S. Timur. *Thin Solid Films*, 520, 1582, 2011.