Conversion treatment of thin titanium layer deposited on carbon steel

Younes Benarioua¹,4*; Bogdan Wendler²; Didier Chicot³

¹ Département de Génie Mécanique, Faculté de Technologies, Université de M’sila, Route de Bordj Bou Arréridj - M’sila 28000, Algérie.
² Institute of Materials Science and Engineering; Lodz University of Technology; 60- 924 Lodz, Poland.
³ Université Lille Nord de France, Lille1, LML, UMR 8107, F-59650 Villeneuve d’Ascq, France.
⁴ Unité de Recherche Matériaux Emergents, Université de Sétif 1- 19000, Algérie

* Corresponding author e-mail: benariouayounes@yahoo.fr

Abstract. The present study has been conducted in order to obtain titanium carbide layer using a conversion treatment consisting of two main steps. In the first step, a thin pure titanium layer was deposited on 120C4 steel by PVD. In the second step, the carbon atoms from the substrate diffuse to the titanium coating due to a vacuum annealing treatment and the Ti coating transforms into titanium carbide. Depending on the annealing temperature a partial or complete conversion into TiC is obtained. The hardness of the layer can be expected to differ depending on the processing temperatures. By a systematic study of the hardness as a function of the applied load, we confirm the process of growth of the layer.

1. Introduction

The use of transition metal carbides and nitrides as coating materials to improve the workpieces surfaces has shown an extensive development in the last years. Among these metallic compounds, titanium carbide presents excellent mechanical and chemical properties as like a high melting point, strong hardness and great chemical and thermal stability under severe conditions [1-7]. Titanium carbide coatings produced by PVD methods have a high hardness and resistance to wear and corrosion but have a low adherence to their substrates [8]. This last behaviour was improved by conversion treatment of titanium and chromium films deposited respectively on carbon steel and cemented steel [9-11].

This work is to examine then how the precipitation of the carbide layer, as a function of the treatment temperature, influences the measurement of hardness under different loads. The deposited titanium film can be transformed into titanium carbide partially or wholly. Several characterization methods show that the growth of the titanium carbide layer takes place from the substrate-film interface towards the coating’s surface.

2. Experimental details

The material of substrates used for this study is 120C4 (AFNOR) steel. The chemical composition in weight is 1.20 % C, 0.11 % Si, 0.21 % Mn, 1% Cr, 0.2 % Ni, 0.01 % Al and 0.09 Cu. The cylindrical samples (diameter 15 mm, height 15 mm) were specularly polished before ionic cleaning and then a pure of thin titanium film (4 μm) was deposited by magnetron sputtering under argon.
atmosphere and a pressure of $3 \times 10^{-3}$ mbar. A description of the deposition technique of titanium films is given in [11]. In order to study the conversion process of titanium film into a titanium carbide one, coated simples were annealed in a tubular furnace at a vacuum of $1.5 \times 10^{-5}$ mbar during 1 h at temperature ranging from 500 to 1100°C.

The structures of films were analyzed using a HZG-3 Bragg–Brentano diffractometer with a monochromatic Co (Kα) radiation. Microstructure of samples (layers/substrates) was performed using an OM of type Olympus B O71 and SEM of type JEOL JSM 35. Further observations were performed on slope cut specimen for which the inclination angle relative to their surface was 2.5°. The samples were polished and etched in a solution composed of 100 ml of water, 2 ml of HF at 40% and 5 ml of $\text{H}_2\text{O}_2$ at 30%. Chemical composition throughout the films and substrates was evaluated using Energy-Dispersive Spectroscopy (EDS). Vickers indentations for loads ranging from 0.1 to 10 N have been applied using a Leco microhardness tester. At least three indentations were performed for each load in order to obtain a significant statistical value of hardness.

3. Results and discussion

3.1. Structure

Fig. 1 shows the X-ray diffraction patterns before and after annealing of titanium deposited on 120C4. It should be noted that for the sample annealed at 500°C, the film presents only titanium in the form of Ti-α. The precipitation of titanium carbide starts at 700°C. The progression of the transformation process increases with the temperature from 700 to 1100°C. The transformation is completed for Ti deposited on the steel at 1100°C.

![Fig. 1: X-ray diffraction spectra of titanium film deposited on 120C4 and annealed at various temperatures.](image)
3.2. Microstructure

The microstructure indicated in fig. 2A, B and C clearly shows the conversion of the film. At 700°C, the titanium carbide is visible as the edge at the film/substrate interface. The precipitation begins at the interface and propagates toward the surface. At 1100°C titanium film is totally transformed in titanium carbide. As indicated by scanning electron microscopy, the transformation of globular cementite into lamellar pearlite begins just then at the interface for low temperature and propagates towards the core of the substrate when the annealing temperature increases.
**Fig. 2:** OM and SEM images of Ti deposited on 120C4 steel after vacuum annealing at temperature 500°C (A), 700°C (B) and 900°C (C).

Fig. 3A and B present the concentration profiles of iron, chromium, titanium and carbon elements obtained by Energy Dispersive Spectrometry of samples annealed respectively at 700 and 1100°C. Carbon diffusion starts to be visible in the sample treated at 700 °C. The gradients Ti and Fe at the film–substrate interface indicated in fig.3A can be considered as artifacts due to lateral resolution intrinsic limitation of the EDS technique. At 1100°C, the analysis demonstrates that the transformation of Ti in TiC is homogeneous over the entire film. The precipitation of titanium carbide occurred can be explained by a large amount of carbon atoms diffused from substrate into titanium layer.
so the results

We notice that there is a significant increase in hardness at 500, 700 and 900 °C whereas measured in film faces with increase of annealing temperature. For the substrates of indentations performed on the substrate. We notice that there is a significant increase in hardness measured in film faces with increase of annealing temperature. For the substrates, the results are similar at 500, 700 and 900 °C whereas at 1100 °C the hardness was increased.

3.3. Hardness
Table 1 collects the results obtained for indentations at the surface of the films and also the results of indentations performed on the substrate. We notice that there is a significant increase in hardness measured in film faces with increase of annealing temperature. For the substrates, the results are similar at 500, 700 and 900 °C whereas at 1100 °C the hardness was increased.

| T(°C) | P (Kgf) | 0.1 | 0.25 | 0.50 | 1   | 2   | 3   | 5   | 10  |
|-------|---------|-----|------|------|-----|-----|-----|-----|-----|
| As deposited Film d (µm) | 6.37 | 10.75 | 16.08 | 24.53 | 36.65 | 46.55 | 62.13 | 89.07 |
|       H (GPa) | 4.54 | 4.01 | 3.58 | 3.08 | 2.76 | 2.57 | 2.40 | 2.37 |
| Subs. d (µm) | 9.45 | 15.15 | 21.30 | 30.03 | 42.61 | 52.60 | 68.06 | 96.61 |
|       H (GPa) | 2.07 | 2.02 | 2.04 | 2.06 | 2.05 | 2.01 | 2.00 | 1.99 |
| 500 Film d (µm) | 6.43 | 11.41 | 17.46 | 26.73 | 39.45 | 49.52 | 65.07 | 93.61 |
|       H (GPa) | 4.49 | 3.76 | 3.04 | 2.60 | 2.39 | 2.27 | 2.19 | 2.12 |
| Subs. d (µm) | 9.26 | 15.07 | 21.56 | 30.64 | 43.23 | 53.84 | 69.30 | 97.23 |
|       H (GPa) | 2.16 | 2.04 | 1.99 | 1.98 | 1.96 | 1.93 | 1.95 | 1.95 |
| 700 Film d (µm) | 5.75 | 10.09 | 15.88 | 24.50 | 37.34 | 47.95 | 63.81 | 92.72 |
|       H (GPa) | 5.62 | 4.75 | 3.67 | 3.09 | 2.64 | 2.43 | 2.28 | 2.16 |
| Subs. d (µm) | 9.46 | 14.90 | 21.14 | 29.79 | 42.28 | 51.72 | 67.69 | 95.56 |
|       H (GPa) | 2.07 | 2.09 | 2.10 | 2.09 | 2.08 | 2.02 | 2.02 | 2.03 |
| 900 Film d (µm) | - | 7.38 | 11.84 | 18.38 | 28.44 | 37.75 | 53.69 | 78.45 |
|       H (GPa) | - | 8.52 | 6.61 | 5.49 | 4.59 | 3.91 | 3.22 | 3.01 |
| Subs. d (µm) | 8.08 | 13.35 | 18.86 | 26.22 | 36.97 | 45.76 | 57.85 | 81.04 |
|       H (GPa) | 2.84 | 2.60 | 2.61 | 2.70 | 2.72 | 2.66 | 2.77 | 2.82 |
| 1100 Film d (µm) | - | - | 7.35 | 11.61 | 17.92 | 22.67 | 30.68 | 44.96 |
|       H (GPa) | - | - | 17.15 | 13.74 | 11.53 | 10.82 | 9.85 | 8.91 |
| Subs. d (µm) | 5.30 | 8.44 | 12.01 | 17.45 | 24.39 | 29.44 | 38.37 | 53.00 |
|       H (GPa) | 6.62 | 6.51 | 6.43 | 6.10 | 6.24 | 6.42 | 6.30 | 6.60 |
In order to visualize the evolution of the hardness with the applied load, it is convenient to use the Meyer’s relation which links the load $P$ as a function of the impression diagonal $d$ as [12].

$$P = a_m d^n$$

Where $a_m$ and $n$ are linked by the dimensional equation and $n$ represents the hardness load dependence.

The use of this relation is not to obtain an intrinsic hardness but to study the annealing effect on the transformation of the film. The results of the tests samples indicated in table 1 can be presented using the relation of Mayer which is only valid in a load domain limited. For this, the resulting bilogarithmic diagrams take linear forms with $a_m$ and $n$ are coefficients. Generally the factor $n$ can take three values. When $n = 2$, the hardness is independent of the load. If $n$ takes values less than 2 ($n < 2$), the hardness increases with the load decreases. In the opposite case ($n > 2$), the composite hardness has to tend to substrate hardness when $P$ tends to infinite values.
We notice that as indicated in the fig. 4, the representation due to Meyer in our case doesn’t show a slope break. A study of thick coatings (100 - 400 μm) of chromium carbide deposited on different substrates has shown that the representation of Meyer shows a break in slope [13].

**Table 2**: Values of Mayer’s coefficient $a_m$ and $n$ of different samples

| Material type | Mayer Coeff. | As deposited | 500°C | 700°C | 900°C | 1100°C |
|---------------|--------------|--------------|-------|-------|-------|--------|
| Subst.        | $a_m$        | 0.121        | 0.129 | 0.121 | 0.159 | 0.367  |
|               | $n$          | 1.97         | 1.96  | 1.97  | 1.99  | 1.99   |
| Film          | $a_m$        | 0.392        | 0.407 | 0.365 | 1.111 | 1.871  |
|               | $n$          | 1.75         | 1.72  | 1.65  | 1.56  | 1.65   |

We will discuss the values of the coefficients $n$ and $a_m$ of the samples presented in tab. 2. For coefficient of films ($n \sim 1.70$) which is less than 2, the hardness measured on the surface of the films increases with the indentation load decreases. For the different charges applied to the substrates, the hardness obtained is constant. This is confirmed by $n$ corresponding to the substrates which equals 2. For the value of $a_m$, it remains constant when there is no transformation up to 700 °C for the substrate and up to 500 °C for the film. For the latter, progresses with the temperature in agreement the progression of the hardness and the metallographic observations on the one hand and X-ray diffraction on the other hand.

**4. Conclusion**

For titanium films deposited by magnetron sputtering on high carbon steel and for different annealing treatments, we have shown that the titanium is transformed into titanium carbide. The growth kinetics of titanium carbide from the substrate / film interface is strongly dependent on temperature. For a treatment time of one hour, we show that the titanium is completely transformed at 1100°C while at 500°C the transformation doesn’t take place. The representation of Meyer, which joins the load applied to the diagonal of the measured imprint, confirms the amplitude of the transformations observed by the metallographic observation and the X-ray diffraction.
We conclude that through a simple methodology of hardness measurement, it is possible to precisely evaluate the growth kinetics of the carbide layer. This method can be validly transposed to diffusion - precipitation studies.

References
[1] Pancielejko M, Pecht W and Czyzniewski A 1999 Tribological properties of PVD titanium carbides Vacuum 53 pp 57-60
[2] Sundgren J E, Jacobson B E and Hibbs M K 1984 Microstructure of nitride and carbide coatings prepared by physical vapor deposition methods Z. Met. kd. 75 pp 855-861
[3] Bromark M, Larsson M, Hedenqvist P, Olsson M, Hogmark S and Bergmann E 1994 PVD coatings for tool application: Tribological evaluation Surf. Eng. 3 p 205.
[4] Shikama T, Shinno H, Fukutomi M, Fujitsuka M, Kitajima M and Okada M 1983 Properties of Ti_{x}C_{1-x} films coated on molybdenum by magnetron sputtering Thin Solid Films 101(3) pp 233-242
[5] Wolfe D E and Singh J 2000 Titanium carbide coatings deposited by reactive ion beam-assisted, electron beam-physical vapor deposition Surf. Coat. Technol. 124 pp 142-153
[6] Storms E K 1967 The Refractory Carbide (New York: Academic Press)
[7] Toth L E 1971 Transition Metal Carbides and Nitrides (New York: Academic Press)
[8] Varacalle Jr D J Lundberg L B Herman H and Bancke G 1996 Titanium carbide coatings fabricated by the vacuum plasma spraying process Surf. Coat. Technol. 86 p 70
[9] Wendler B and Benarioua Y 1993 Vacuum annealing study of thin Ti layers on high carbon steel substrates Pro. Int. Conf. on Applied Crystallography (Katowice) World Scientific (Publishing Co. Pte. Ltd) pp 228-230
[10] Benarioua Y, Lesage J, Bemporad E and Chicot D 2006 Titanium carbide films obtained by conversion of sputtered titanium on high carbon steel Surf. Coat. Technol. 200 pp 5447-5454
[11] Benarioua Y, Boubaya R, Lesage J and Chicot D 2013 Annealing study of thin chromium layers on cemented steel substrates Surf. Coat. Technol 227 pp 65-69
[12] Meyer E 1908 Phys. Z. 9 p 66
[13] Chicot D and Lesage J 1995 Absolute hardness of films and coatings; Thin Solid Films 254 pp 123-130