CHARACTERIZATION OF THIN TITANIUM FILMS DEPOSITED ON STEEL SUBSTRATES OBTAINED BY MAGNETRON SPUTTERING METHOD

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ملخص : عرفت كربيدات التيتان بأهميتها العلمية و التكنولوجية الكبيرة. تكمن أهمية تطبيقاتها الواسعة في صلادتها العالية و خواصها الحرارية و المعدنية. درسنا في هذا البحث تأثير المعالجات الحرارية (400-1000°C) على التفاعل بين طبقات رقيقة من التيتان و مساند فولاذية من النوع 100C6 حسب تقويم (AFNOR) الحاوي على 1 % كتلة من الكاربون, تم ترسيب الطبقات بواسطة الرش المهبطي عند الدرجة 200°C . تمت الدراسة و التحليل بإستعمال إنعراج الأشعة السينية (XRD) و مطيافية إلكترون أوجي (AES) و المجهر الإلكتروني الماسح (SEM) قياسات الصلادة للعينات المعالجة حراريا بينت إرتفاعها مع درجة الحرارة حتى القيمة العظمى ($3500\ kg/mm^2$) ثم إنخفاضها تدريجيا. إرتفاع الصلادة ناجم عن إنتشار الكاربون و تشكيل كربيد التيتان بينما إنخفاضها مرتبط بإنتشار الحديد و تكون أوكسيد الحديد (Fe_2O_3) . عند درجات الحرارة العالية لاحظنا تشكل أوكسيد التيتان (TiO_2).

كلمات دالة : الطبقات الرقيقة, الترسيب, PVD, التيتان, الحديد, التحليل.

ABSTRACT: Titanium carbides are well known materials with great scientific and technological interest. The applications of these materials take advantage of the fact that they are very hard, refractory and that they have metallic properties.

In this work, we have studied the influence of the heat treatment temperatures (400-1000°C) on the interaction between the titanium thin films and steel substrates. Steel substrates, 100C6 type (AFNOR norms), containing approximately 1 wt % of carbon, were coated at 200°C with titanium thin films by magnetron sputtering.

The samples were characterized by X ray diffraction (XRD), Auger electron spectroscopy (AES) and scanning electron microscopy (SEM). Vikers micro-hardness measurements carried out on the annealed samples showed that the micro-hardness increases with annealing temperature, reaches a maximum ($3500\ kg/mm^2$), then decreases progressively. The growth of micro-hardness is due to the diffusion of the carbon, and to the formation of titanium carbide. However, the decrease of micro-hardness is associated to the diffusion of iron and the formation of iron oxide (Fe_2O_3). At higher temperatures, we note the formation of titanium oxide (TiO_2).

KEY WORDS: Thin films, Deposition, PVD, Titanium, Steel, Characterization.

1. Introduction

Thin films technology knew an accelerated development of their applications in many domains (microelectronics, protection against the oxidization and corrosion, solar cells, thermal insulation and decoration, etc.).

The transition-metal carbides are a class of very hard materials. These compounds are of great scientific and technological interest. The titanium carbides belong to the class of the so-called refractory metal compounds, used extensively as coatings in the technology at high temperature because of their physicochemical properties, particularly, high thermal stability and good resistance against the corrosion as showed by Teghil [1]. TiC and TaC thin films are used for the first time in applications of thermocouple at high temperatures by Bhatt [2]. Most application of the transition metal carbides rely upon their extreme hardness; for example, they are widely used as the main constituent in metal cutting tools, as mentioned by Mitsuo [3]. Furthermore, they have high melting points and extreme hardness, as covalent crystals, and a NaCl structure. Méçabih [4] showed that this combination of properties has made the carbides important in a wide variety of technological applications, and the light weight of TiC has made it particularly attractive for aerospace applications.

In this work, we elaborate thin films of titanium carbides by deposition of pure titanium thin films on steel substrates by magnetron sputtering method, then by heat treatments under vacuum. It forms titanium carbides following the diffusion of carbon from substrate to thin film. The interaction between the titanium thin films and substrates is studied by x ray diffraction (XRD), Auger electron spectroscopy (AES), and scanning electron microscopy (SEM).

2. Experimental procedures

The substrates used in these experiments were samples of steel type: 100C6 (1 %C; 0.3 %Si; 0.3 %Mn; 0.025 %P; 0.025 %S; 1.4 %Cr; 0.3 %Ni). The substrates, in the shape of a disk of 10 mm diameter and 1 mm in thickness, were polished mechanically and then ultrasonically cleaned consecutively with trichloroethylene, acetone, and methanol. Finally the substrates were submitted to ionic bombardment cleaning by Ar ions (289 V, 1 A, 4 min). Prior to Ti deposition, the target was cleaned by sputtering for about 10 minutes with a shutter covering the substrates. Titanium thin films (0.8µm thickness) were deposited under vaccum (~10^{-4} mbar) by magnetron sputtering with RF power = 200W, and temperature of substrates = 200°C, during 1 hour of deposition, from a target of titanium (99.99 % purity). In order to activate the reaction between substrate and the thin films, samples were subjected to high vacuum annealing (10^{-4} mbar) at a temperature between 400 and 1000°C for one hour. For the comparison, a series of uncoated substrates were heat treated in the same temperature interval. To characterize samples before and after thermal treatment, the x-ray diffraction, Auger electron spectroscopy, and scanning electron microscopy were used.

3. Results and discussion

3. 1. Analysis by x-ray diffraction

The x-ray (CuKα Ni-filtered radiation) spectrum from 100C6 substrates before annealing is shown in figure 1. The spectrum showed that the substrates are constituted of Fe_{α}, Fe_3C phases. However, the spectrum from 100C6/Ti sample before thermal treatment, figure 2, show that in addition of iron and Fe_3C, the apparition of titanium characteristic peaks with reduction in the number and intensity of the substrate peaks. This last observation confirms that the deposited films are constituted of pure titanium.

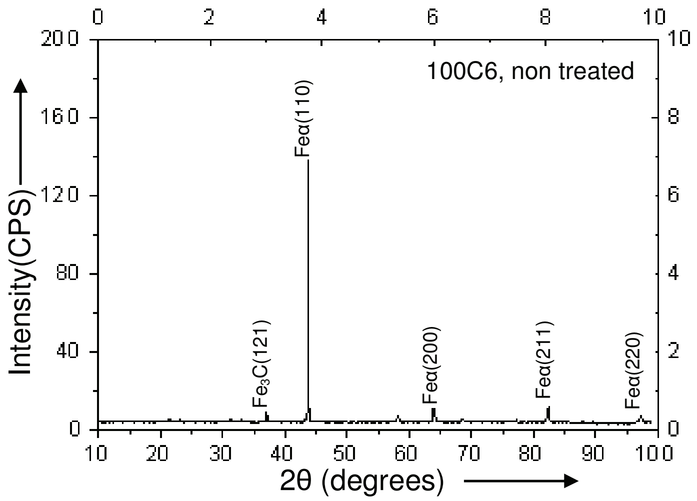

Figure 1: XRD spectrum from substrate 100C6.

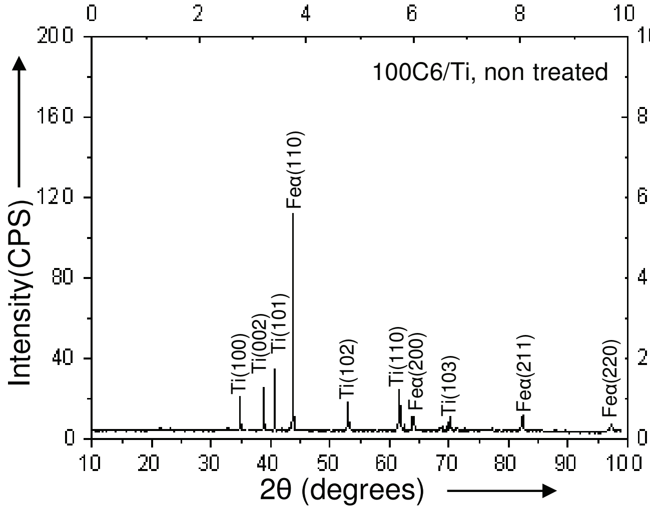

Figure 2: XRD spectrum from sample 100C6/Ti, before annealing.

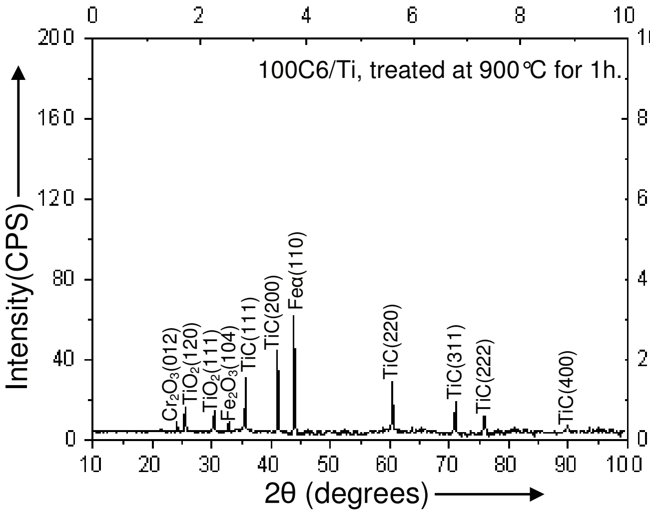

Figure 3: XRD spectrum from sample 100C6/Ti, heat-treated at 900°C for 1h.

The XRD spectra from samples treated at the temperature interval of 400 to 1000°C for one hour, show a progressive reduction in intensities and number of titanium peaks and substrate phases, and on the other hand, a progressive increase in intensities and number of the titanium carbide (TiC) reflections. This phase has no preferential orientation. We also notice the apparition of iron, titanium and chromium oxides at high temperatures (Fig. 3).

Since titanium has higher efficiency to carbon than both Cr and Fe, the formation of TiC is due to the reaction between carbon from substrate and titanium thin film. It results a consumption of the titanium layer and the increase of TiC peaks in number and intensity with annealing temperature. The apparition of iron, titanium and chromium oxides, Fe_2O_3, TiO_2, Cr_2O_3, is probably caused by insufficient applied conditions during the thermal treatments (insufficient vacuum) particularly at higher temperatures, were the formation of these oxides is favored. This may indicate that these films have an open structure with voids along the grain boundaries. The same structure has been observed for TiN by Al-jaroudi [5].

3. 2. Auger electron spectroscopy

AES depth profiles of 100C6/Ti sample before annealing are shown in figure 4. Because of the natural oxidation of titanium film during their storage at room temperature before AES analysis, one observes a high content of carbon and oxygen in the superficial region of the samples. After elimination of the contaminated layer, the titanium film seems have a relatively high purity and a constant concentration up to the interface. This justifies the homogeneity of thin films achieved by the magnetron sputtering method. The slight increase of the oxygen content at the interface is caused either by the adsorption of the oxygen on the substrate surface before the Ti deposition or by its incorporation into the Ti layer during the deposition process. Gheriani [6] showed the effect of substrate surface ion bombardment etching on reaction between thin films and substrates.

Figure 5 shows AES profiles of 100C6/Ti samples heat treated at 700°C during 60 minutes. It reveals that the titanium concentration decreases significantly and that of carbon increases. This fact leads to the reaction of these elements and to the formation and growth of TiC carbide. It can be also noted the diffusion of Ti towards the steel substrate, and carbon and iron towards the thin coating layer.

In the rich region in Ti, up to 60 minutes of ion etching with argon ions, we observe that the titanium concentration decrease progressively with a low speed. However, in the region from 60 to 85 minutes of sputtering, we note a speed decrease in titanium concentration. We can say that the reaction starts at the substrate- titanium film interface, and then develops towards the superficial layers of the sample, as observed in Gheriani [7] work.

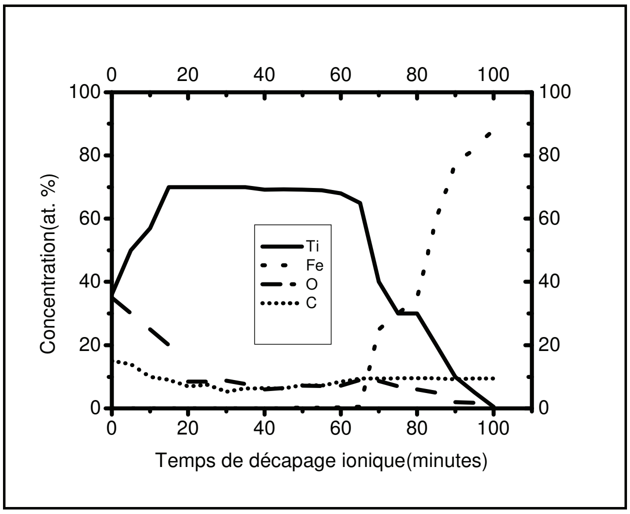

Figure 4: AES depth profiles of 100C6/Ti sample, before annealing.

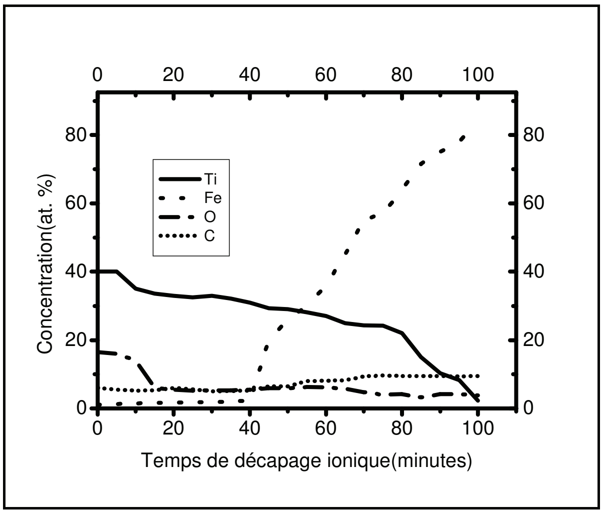

Figure 5: AES depth profiles of 100C6/Ti sample, heat treated at 700°C during 60 min.

3. 3. Scanning electron microscopy analysis

Figure 6, shows a scanning electron micrograph from the surface of coated sample annealed at 400°C for 1 hour. The surface morphology revels that the Ti film had a dark gray color, consisting of particles homogeneously distributed. However, in the case of the sample annealed at 900°C for 1 hour, it is observed the apparition of voids and white particles distributed randomly on the surface (Fig. 7).

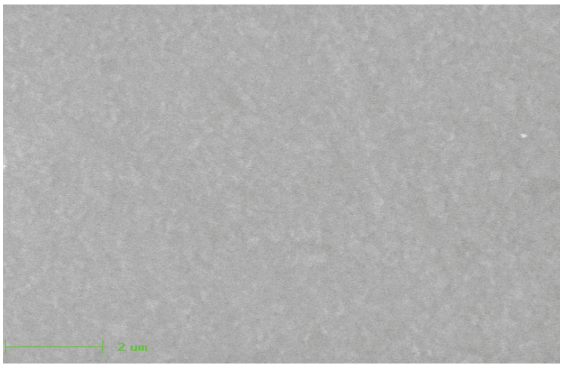

Figure 6: SEM micrograph of the 100C6/Ti sample annealed at 400°C for 1h.

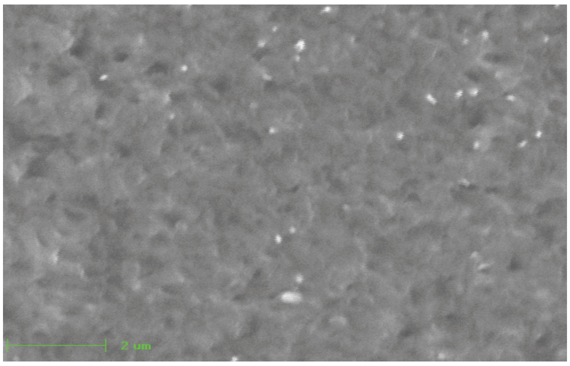

Figure 7: SEM micrograph of the 100C6/Ti of the sample annealed at 900°C for 1h.

3. 4. Micro-hardness measurement

Micro hardness tests were performed by Vickers method under small load (40g). Figure 8 represents the micro-hardness variation with annealing temperature for substrate and coated samples. One notices for the curve corresponding to the substrate, an increase of the micro-hardness until a maximum value of 600 Kg/mm^2 at 700°C, then a relatively soft decrease. However, the micro-hardness values of coated sample are more important and reach their maximum of 3200 Kg/mm^2 at 900°C, then begin to decrease. The observed increase of the micro-hardness with annealing temperature is due to the formation and the growth of titanium carbide. However, the reduction of the micro hardness after the maximal value is probably caused by the effect of soft ferrite formation beneath of the TiC layer, since carbon diffuses from region lying near the substrate surface. So, when hard TiC layer is laying on soft ferrite, during the micro hardness measurements (even when using small charge P = 40 g) ferrite is deformed and it results in reading of smaller values of micro hardness. Besides, the formation of iron, titanium and chromium oxides can also contribute to the decrease of the micro hardness.

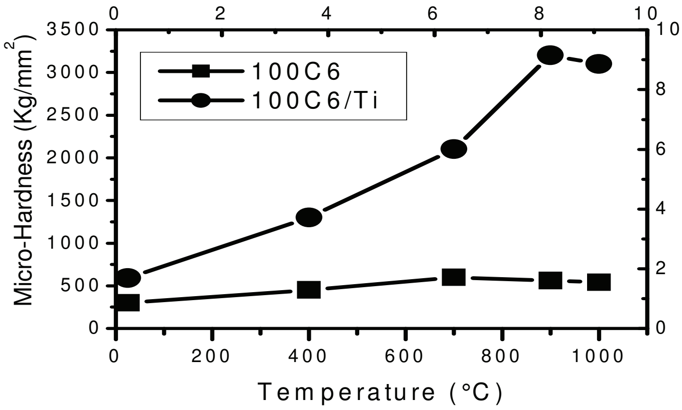

Figure 8: Variation of micro-hardness with annealing temperature.

4. Conclusion

Titanium carbide coatings are obtained from a film of titanium deposited by magnetron sputtering method on steel substrates (1%wt of carbon content) and annealed in vacuum at different temperatures. TiC is forming by high diffusion rate of carbon from substrate towards titanium thin film in the studied temperature range. The formation of titanium carbide is accompanied by an important increase of the micro-hardness.

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