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Formation of Ti(OCN) Layers Under Glow Discharge Conditions

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Abstract. By using a gaseous mixture composed of tetraisopropoxytitanium, nitrogen and hydrogen in PACVD process, we obtain Ti(OCN) layers of a good performance properties, such as a high hardness and good resistance to corrosion and to frictional wear. The optimum temperature of the process is 500°C. At higher temperatures, the surface microhardness decreases. When the process is carried out at 700°C, a surface layer which contain titanium cannot be obtained, only a diffusive oxycarbonitrided layer forms. Spectral investigations by optical emission spectroscopy have shown that the active particles that take part in the formation of the Ti(OCN) type layer are titanium ion Ti^+ , nitrogen particles: N , N_2^+ , NH , oxygen atoms and CN radicals coming from the gaseous atmosphere and also nitrogen from the pre-nitrided substrate.

1. INTRODUCTION

A surface layer commonly produced by the CVD method is titanium nitride (TiN). The titanium donor is usually titanium tetrachloride-TiCl₄. The process is conducted at a temperature above 600°C (the PACVD method) [1], since the layers produced at lower temperatures contain chlorine which worsens their useful properties [2]. This is why the chlorine atmospheres tend to be abandoned in the CVD processes, and also a side product of the reaction here is hydrochloric acid. Recently, metallorganic compounds have become the donors of the elements involved in the reaction, especially in the PACVD process. Rie and Gebauer [3] have shown that TiCN surface layers can be produced from titanium tetradimethylo- and tetradiethyloamides at a temperature as low as 400°C. Stock and Mayr [4] obtained Ti(OCN) layers by using a mixture of tetraisopropoxytitanium, hydrogen and nitrogen under glow discharge conditions. The same gaseous atmosphere used in a CVD process without electrical activation of the environment gives a TiO₂ layer [5]. Our earlier studies [6,7] have shown that layers of the Ti(OCN) type produced from a mixture of tetraisopropoxytitanium vapours, H₂ and N₂ by glow discharge enhanced CVD have a surface hardness of the order of 1800 HV 0.05 and good resistance to corrosion and to frictional wear. In the present study, we examined how the formation of a Ti(OCN) layer depends the temperature of the substrate and the presence of nitrogen in the prenitrided substrate.

2. EXPERIMENTAL METHODS

The surface layers were produced in a typical PACVD apparatus [6]. The DC plasma was applied. The samples were the cathode and they were heated by action of low-temperature plasma i.e. bombardment of the substrate surface by positive ions. This process also activates the surface to be coated. The substrate was Armeo iron (0.05% C). The gaseous atmosphere was composed of Ti(OiC H₃)₄ vapours mixed with hydrogen and nitrogen, or with H₂ alone when the substrates were prenitrided. Part of the

samples were prenitrided in the $H_2 + N_2$ atmosphere under glow discharge conditions. The layers were examined metallographically and their surface Vickers hardnesses were measured using the Hanneman hardness testing machine. The chemical composition of the $Ti(OCN)$ layers was determined using a Cameca SU-30 X-ray microanalyzer. The spectrum of the $Ti(OiC_3H_7)_4 + H_2 + N_2$ mixture was examined by optical emission spectroscopy. The four experiments were done, the temperatures of them were 500, 560, 600, and 620°C. The temperature of the sample which was also the cathode raised from room temperature by increasing plasma power and after that the mixture was introduced into the interelectrode space. The plasma spectrum emitted perpendicularly to the axis of the electrode system was recorded using a PGS-2 spectrograph (with a focal length of 2m). The spectrum was photographed in the first order of reciprocal linear dispersion of 0.7nm/min. The spectral range was from 200 to 600nm [8].

3. RESULTS AND DISCUSSION

Irrespective of the steel substrate $Ti(OCN)$ layers of the greatest thickness of about $10\mu m$ and the surface hardness of about 1800 HV 0.05 form at a temperature of 500°C. When the temperature is increased, the thickness and the surface hardness of the $Ti(OCN)$ layers decrease, which is associated with their changed chemical composition (an increased content of oxygen and carbon). The layers become porous and their thickness is nonuniform. When the temperature is 700°C an adhesive layer which contain titanium ($Ti(OCN)$) cannot be observed, but only a diffusive oxycarbonitrided layer is formed [6]. Hence, the treatment temperature is an essential parameter that determines the type and the properties of the growing layer. We have studied this effect by examining the spectra of the $Ti(OiC_3H_7)_4 + H_2 + N_2$ mixture under glow discharge conditions using the optical emission spectroscopy method. Atomic and molecular species, both neutral and ionized (Ti , Ti^+ , N , H , C , H_2 , O , N_2 , N_2^+ , CN , NH) have been identified in plasma spectrum. Fig. 1 shows for example the variation of the radiation intensity of some selected particles that can take part in building up the layer.

Figure 1. Variation of the radiation intensity of selected spectral lines as a function of the cathode (sample) temperature [8].

We can see from this figure that, above 560°C, the emission intensity of the Ti^+ ions (Ti II) obtained from the gaseous atmosphere, that could be responsible for the formation of the $Ti(OCN)$ layers, decreases. As the temperature increases, the intensity of the spectral band due to CN particles also obtained from the gaseous atmosphere increases and this can be attributed to the carbonitriding process which occurs in higher temperatures. It is true that, above 560°C, the spectral intensity of Ti atoms (Ti I), which can originate from $Ti(OCN)$ layer increases, but this can be explained in terms of the ion sputtering of the thin porous $Ti(OCN)$ layer that form at a temperature of 600°C. This explanation is confirmed by the presence of atomic iron (Fe I) in the plasma above 600°C, which can be only

attributed to the sputtering of the steel substrate. We can, thus, conclude that, when producing Ti(OCN) layers from $\text{Ti}(\text{O}i\text{C}_3\text{H}_7)_4$ a temperature of 560°C should not be exceeded.

An essential role is also played by nitrogen contained in the nitrided steel substrate. In our previous work [6,7] we establish that the wear and corrosion resistance of the Ti(OCN) layer is better when the substrate is nitrided using glow discharge conditions. Nitrogen in the prenitrided substrate is active in the formation of the Ti(OCN) layer improving the adhesion and properties of the nitrided + Ti(OCN) composite layers. It was confirmed by our experiment on the formation of a Ti(OCN) layer on prenitrided Armco iron with a nitrogen-free reactant mixture. Fig. 2. shows the microstructure of the layer thus produced, whose surface hardness was 1550 HV 0.05.

Figure 2. Microstructure of a Ti(OCN) type layer formed on Armco iron in the atmosphere composed of $\text{Ti}(\text{O}i\text{C}_3\text{H}_7)_4$ vapours and H_2 .

A qualitative examination of the composition of these layer has confirmed that nitrogen is present in it. The chemical compositions of the Ti(OCN) layers produced on Armco iron, both without and glow-discharge prenitrided, were also examined quantitatively. The analysis has shown that nitrogen present in the substrates participated in the formation of the layers. The results of the examination (in at.%) are given in Table 1.

Table 1. Chemical composition of Ti(OCN) layers produced on without and prenitrided Armco iron in the $\text{Ti}(\text{O}i\text{C}_3\text{H}_7)_4 + \text{H}_2 + \text{N}_2$ atmosphere.

Ti(OCN) layer	Ti	N	O	C
produced on Armco iron	36	23	30	11
produced on prenitrided Armco iron	34	28	26	12

It should also be noted that the carbon content in the Ti(OCN) layer is relatively low (11 at.%), in spite of its high content in a tetraisopropoxytitanium molecule. This may be attributed to the small number of active carbon particles present in the plasma. But we must also remember about the presence of atomic oxygen which can be obtained from decomposition of tetraisopropoxytitanium and may contribute to the film growth.

Based on the results of our experiments we wish to propose a general scheme of the formation of a Ti(OCN) layer from the mixture composed of a titanium tetraisopropoxide vapours, hydrogen and nitrogen using PACVD method under glow discharge conditions (Fig. 3).

Ti(OiC ₃ H-) .	N ₂ + H ₂ :	gaseous atmosphere
C, Ti ⁺ , CN ₂ , O,	N ⁺ , NH, N ₂ ⁺ , N,	main active particles obtained under glow discharge conditions
Ti(OCN)		surface layer
N		prenitrided substrate

Figure 3. General proposal of the formation of a Ti(OCN) layer from a mixture of Ti(OiC₃H₂)₄ + H₂ + N₂ by the PACVD method under glow discharge conditions.

The process temperature: - **500°C** - the Ti(OCN) layer formed has the highest surface hardness and the greatest nitrogen content; the particles that play here the decisive role are: Ti⁺, O, N⁺, NH, N₂⁺ and N. - **600°C** - a Ti(OCN) layer form but is nonuniform; its thickness is about 3µm, the nitrogen content in it is small (up to 15 at.%) and the oxygen content is high (up to 40 at.%). The decisive role in the layer formation is played by: Ti⁺, O, C and CN particles. At this temperature, the ion sputtering process takes place; titanium (Ti) and iron (Fe) atoms are present (Fig. 1).- **700°C** - the layer formed is oxycarbonitrided one; the dominant active particles are: CN, C, N, NH, N₂⁺ and N.

4. CONCLUSIONS

When the treatment is carried out at a temperature of 500°C, the Ti(OCN) layer obtained is finecrystalline and its predominant constituent is titanium nitride TiN whose lattice parameter ranges from 0.423nm to 0.420nm. It differs from the value of pure TiN 0.424nm because of the presence of oxygen. The appearance of the surface of the layer is shown in Fig. 4. It should be noted that, in the formation of the Ti(OCN) layer, an essential role is played by the cathode sputtering effect, especially during the time when the treated parts are heated to the process temperature. This effect increases the development of the treated surface and the structural defects at this surface zone. The plasma acting upon the surface layer of the treated surface increases its surface energy, which, in turn, facilitates the chemisorption of the active particles that build up the layer and also, thanks to the good affinity of nitrogen to titanium, enhances the diffusion of nitrogen from the prenitrided substrate into the layer. As a result, the growing Ti(OCN) crystallites are uniform and finegrained.

Figure 4. The appearance of the surface of a Ti(OCN) layer formed on prenitrided Armco iron at a temperature of 500°C.

Figure 5. Diffractogram and the appearance of the surface of a Ti(OCN) produced on Armco iron at a temperature of 600°C .

At a temperature of 600°C , the Ti(OCN) layer formed has a multi phase TiO_2 , TiN structure with the predomination of the TiO_2 phase. A diffractogram of such layer and the appearance of its surface are shown in Fig. 5. The layer contains microcracks caused most probably by the considerable residual stresses developed during the growth of its multiphase structure. The layer is nonuniform and porous. At a temperature of 700°C , the particles which predominate are CN particles (Fig. 1) and the active particles present in the nitrogen + hydrogen atmosphere under glow discharge conditions, i. e. NH , N , N^+ , N_2^+ [9,10]. The process consists of oxycarbonitriding (atomic oxygen is present due to the decomposition of tetraisopropoxytitanium).

Using an excessive amount of tetraisopropoxytitanium (above 4 vol.% in the gaseous mixture) we obtain a multiphase layer composed of TiO_2 , Ti(OCN) and amorphous carbon on the surface.

Recapitulating, we can say that the conditions advantageous for the formation of a Ti(OCN) layer occur when the treated surface is activated (by the cathode sputtering effect during the heating of the treated parts) and when the substrate has been prenitrided, since this permits controlling the earliest stage of the formation of the Ti(OCN) layer. Ti(OCN) layers with a high nitrogen content can be obtained at 500°C when the $\text{Ti(OiC}_2\text{H}_5)_4$ vapour content in the gaseous atmosphere does not exceeded 4 vol.%.

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