THE GROWTH MODEL OF THE Ti(NCO) LAYER PRODUCED
BY PACVD METHOD FROM A METALORGANIC
TITANIUM COMPOUND

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Abstract

The paper specifies the conditions under which the Ti(NCO) surface layers from
titanium tetrabutylammonium can be produced on steels. It also describes the
influence of hydrogen from the atmosphere and nitrogen from the nitrided
substrate on the chemical composition of the surface layers. The model of layer
growth is proposed according to the mass spectral investigations of the decomposition
of titanium tetraisopropoxides, and to results of spectral investigation of the plasma
mixture containing Ti(OC₃H₇)₄ + H₂ + N₂ as a function of process temperature using
optical emission spectroscopy and plasma diagnosis of nitrogen + hydrogen atmosphere.

1. Introduction

The Chemical Vapour Deposition (CVD) methods have been widely used in industry
for producing coatings resistant to wear and corrosion. A common feature of the CVD
methods is that they give surface layers from the chlorides such as e.g. TiCl₄ in the case of
TiC, TiN and Ti(CN) coatings [1,2]. Traditional CVD processes must be carried out at high
temperatures at which the chemical reactions involved in the formation of the coatings can
take place. This requirement restricts the application range of these processes. The PACVD
method, carried out under glow discharge conditions in a gaseous atmosphere with a content
of metal-organic compounds such as vapours of tetrabutylammonium Ti(OC₃H₇)₄ [2-4],
tetraethyloamide Ti[N(C₂H₅)₂]₄ or tetradimethyloamide Ti[N(CH₃)]₄ [5] is expected to
have a successful future and to gain broad applications. Using these vapours at a temperature
of about 500°C, we can produce the Ti(NCO) or Ti(CN) type coatings at a temperature of
about 500°C. By changing the process parameters (in particular the temperature) and the
composition of the Ti(OiC₃H₇)₄ vapour enriched reactive atmosphere during the glow
discharge assisted process, we can produce layers with various contents of carbon, oxygen
and nitrogen and thereby modify the properties of the layers. The three phases TiO, TiN and
TiC which are constituents of the coating, have the same crystalline structures of the NaCl
type and show an unlimited mutual solubility [6]. The aim of the study was to propose a
model of the formation of titanium oxyxocarbonitride Ti(NCO) layers by the glow discharge
assisted MOCVD method using the Ti(OC₃H₇)₄ vapours mixed with hydrogen and nitrogen.
2. Experimental methods

The process was carried out in a PACVD apparatus, designed and constructed at our Faculty [2]. Since the boiling temperature of tetraisopropoxytitanium is relatively high (50°C/1hPa), the way in which this compound is fed to the reactor should be heated. The substrate was Armco iron, without and subjected to glow discharge nitriding to produce a diffusive nitrided zone. The Ti(NCO) layers were produced at a temperature of 500°C using a gaseous atmosphere composed of Ti(OiC$_3$H$_7$)$_4$ (the content of the organic compound was 5% by volume) mixed with nitrogen and hydrogen. The glow discharge was triggered from a D.C. power supply unit. The parameters of the PACVD processes were constant and equal to: $T=500^\circ C$, $t=2h$, $p=4hPa$.

The processes performed were of two types. The process of the first type was conducted without the participation of hydrogen in the gaseous mixture, so as to eliminate its effect on the layer formation. Process of the other type, on the other hand, used a nitrogen-free gaseous atmosphere which permitted examining the role of the nitrogen released from the glow discharge prenitrided substrate; the nitriding process parameters were: $T=520^\circ C$, $t=4h$, $p=4hPa$, $N_2/H_2=1/10$.

The distribution of the elements in the Ti(NCO) layers was measured by the Glow Discharge Optical Spectroscopy method using a Jeol 505 apparatus whose resolution was 20nm, voltage - 0.7 kV and current - 30 mA.

A special attention was paid to spectral examinations of the titanium tetraisopropoxide vapours mixed with nitrogen and hydrogen under glow discharge conditions. A sample made of stainless steel was the cathode and it was heated by glow discharge. The sample temperature was varied from 500 to 620°C. The mixture of tetraisopropoxide, nitrogen and hydrogen was introduced into the space between the electrodes. The optical emission spectroscopy (OES) method was used for examination [7]. Plasma spectrum emitted perpendicularly to the axis of the electrode system was recorded by the 2m plane grating spectrograph PGS-2. The spectrum was photographed in the first order at a reciprocal linear dispersion of 0.7 nm/min. The spectral range was from 200 to 600 nm.

In order to determine the sequence of the chemical bond disintegration in the Ti(OiC$_3$H$_7$)$_4$ molecule, the fragmentation of this compound was examined by mass spectrometry using an MS AB Jeol apparatus. The samples were evaporated at a temperature increasing from 30 to 300°C at a rate of 30°C/min in a vacuum of $10^{-5}$hPa.

3. Results

Fig.1 shows the distributions of the elements present in the titanium oxycarbonitride layers produced in various reactive atmospheres at a temperature of 500°C. As can be seen in this figure, the titanium oxycarbonitride layer produced on a prenitrided substrate in a gaseous atmosphere composed of tetraisopropoxytitanium + hydrogen+ nitrogen contains the greatest amount of nitrogen and the smallest amount of oxygen. With the hydrogen-free reactive atmosphere, the amount of oxygen in the Ti(NC)) layer increases, whereas the amount of nitrogen decreases. Hence we can conclude that hydrogen present in the gaseous mixture not only promotes the decomposition of tetraisopropoxytitanium, but also binds the oxygen from the gaseous mixture to form a water molecule. In the layer produced in a nitrogen-free atmosphere, the dominant component is oxygen. When using the Ti(OiC$_3$H$_7$)$_4$ + H$_2$ atmosphere, the presence of nitrogen in the Ti(NCO) layer can only be explained in terms of its diffusion from the nitrided layer. The participation of nitrogen from the nitrided layer in
the formation of TiN layers in the CVD processes carried out in TiCl₄-containing atmospheres has already been reported in the literature [8,9].

**Fig. 1.** Distribution of the concentration of the elements in the Ti(NCO) layers produced in various gaseous mixtures: a) N₂+Ti(OiC₅H₇)₄, b) H₂ + N₂ + Ti(OiC₅H₇)₄ on a prenitrided substrate c) H₂ + Ti(OiC₅H₇)₄ on a prenitrided substrate.
Examinations of the chemical composition of the low-temperature plasma of the reactive mixture employed revealed the presence of the atomic and molecular species (both neutral and ionised): Ti, Ti", N, H, C, H₂, N₂, N₂", CN, NH [10] in the plasma spectrum. It has been shown that Ti" ions responsible for the formation of the Ti(NCO) layer occur within the temperature range from 480 to 560°C and their content decreases above a temperature of 560°C. As the temperature increases, the intensity of the spectral band due to CN particles increases and this can be related with the carbonitriding process. It is true that, above 560°C, the spectral intensity of Ti atoms increases, but this can be explained by the ion sputtering of the Ti(OCN) layer which forms under these conditions. This explanation has been confirmed by the presence of atomic iron in the plasma above 560°C, which can only be attributed to the steel substrate being sputtered. We can thus conclude that, when producing Ti(OCN) layers from Ti(OiC₃H₇)₄ at a temperature of 560°C should not be exceeded.

Fig. 2 shows a mass spectrogram illustrating the intensities of the ions formed through the fragmentation of the Ti(OiC₃H₇)₄ depending on their molar mass.

![Mass spectrogram of the fragmentation of tetrakisopropoxysilane](image)

Fig.2. Mass spectrogram of the fragmentation of tetrakisopropoxysilane

By analysing Fig.2, it can be seen that the decomposition of Ti(OiC₃H₇)₄ begins from the split off a hydrogen atom resulting in an ion of a mass of 238 being formed, described by the formula TiC12H27O4+. Then a CH₂ group splits off, yielding an ion of a mass of 269 and formula as shown in the figure. The next group to split off is an OCH(CH₃)₄ group giving an ion of a mass of 225. The final product of the decomposition is a Ti+ ion with a mass equal to 43, formed from the TiO+ ion (mass=64) as a result of atomic oxygen being eliminated. The decomposition sequence is consistent with the earlier data on the decomposition of metal alcoxides reported by Breibarth [11].
4. Conclusions

The results of our studies suggest that the active molecules responsible for the formation of the Ti(NCO) type surface layer are:

- atomic oxygen, Ti+ and TiO+ ions formed as a result of the decomposition of tetraisopropoxytitanium,
- N* atoms, NH* radicals and the N+, N2+ and NH+ ions formed in the nitrogen and hydrogen mixture under glow discharge conditions - an effect described in connection with the glow discharge assisted process [2,7,12],
- CN molecules formed during the process,
- atomic nitrogen from the (Fe(N) phase of the nitrided substrate, which improves the adhesion of the Ti(NCO) coating being formed by giving it a diffusion character.

Fig. 3 shows a model of the growth of the Ti(NCO) type layer in a Ti(OiC3H7)4 + H2 + N2 vapour mixture. The model indicates unequivocally that, by changing the process parameters, primarily the chemical composition of the reactive mixture and the temperature, we can modify the chemical composition of the layers and thus their performance properties. It should be emphasised that the composite layer of the nitrided layer +Ti(NCO) type produced under the optimum process parameters is characterised by a high surface hardness of about 2050 HV 0.05, a good corrosion resistance and a good frictional wear resistance [3].

![Diagram of the growth model of the Ti(NCO) layer](image)

Fig.3. Growth model of the Ti(NCO) layer produced by PACVD method under the glow discharge conditions using a mixture of tetraisopropoxytitanium, nitrogen and hydrogen
Acknowledgements
These investigations are supported by the Polish State Committee for Scientific Research - project no PBZ-KBN-15/T09/99

References