Peculiarities of Titanium Compound Films Formation on Heat Sensitive Substrates by Electric Arc Vaporization

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ABSTRACT

Peculiarities of nitride, oxide and carbon films deposition onto plastic and other heat sensitive substrates by arc vaporization at temperatures not exceeding 30-40 °C have been considered. Variation of properties of the formed film depending on partial pressures relationship of reactive and inert gases is considered by example of titanium nitride. A special attention is paid to energy processes in plasma. In the case of titanium oxide formation utilization of carbon dioxide results in the possibility of the layer deposition at the expense of titanium reduction on the cathode and decrease of its surface oxidation.

INTRODUCTION

Broad application of titanium compounds for various areas of engineering is well-known. Most works deal with titanium nitride, used as hard coating, barrier layer in electronics, wear resistant and antifriction coating. Titanium oxide layers are use mostly for optical purposes. For many years magnetron sputtering and activated reactive EB evaporation have been main methods of titanium compounds deposition. Arc vaporization method has been used up to this day very insignificantly, mainly for the deposition of wear resistant coatings at temperatures of the substrate 150-400 °C. Basically it is preconditioned by the droplet phase in the vapor, which affects the film surface properties significantly, sharply reducing applicability of the method in electronics, optics and hard coatings. High thermal loads on the substrate is the second problem. As a matter of fact, the second drawback was long ago converted into an advantage and arc discharge is uses for preliminary cleaning and heating of the substrates before hard layers deposition. However, detailed study of arc discharge behavior during operation in a mixture of various gases permits somehow to change the attitude to the coatings of titanium compounds for practical purposes.

In the present work peculiarities of formation of titanium compound layers in the medium of various gases, properties of such layers and probable areas of application are considered.

EXPERIMENTAL DETAILS

Usually the arc discharge takes place in vacuum without additional gas admittance, as the arc lives at the expense of metal vapors [1, 2]. To deposit chemical compounds reactive gas is used and its pressure is determined by relationship of metal and gas vapors, necessary for a certain compound. However, additional admittance of inert gas (argon, helium) changes the character of the discharge essentially and as a consequence the property of the deposited film is changed. The chamber dimensions influence the process essentially. The experiments were carried out in industrial scale chamber 800 mm in diameter and 1 m long. A U-shaped cathode of straight length 1500 mm was mounted in the center of the chamber. The vacuum chamber body served as an anode.

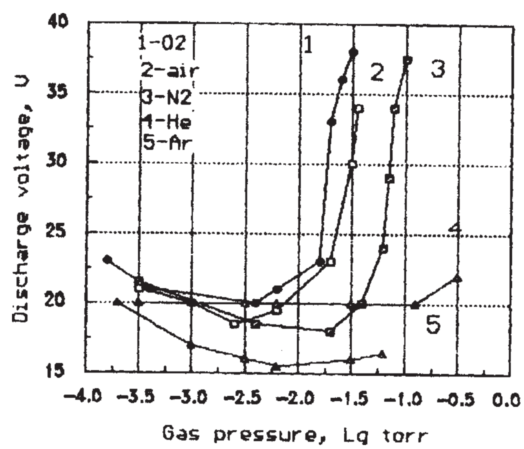

Figure 1. Discharge voltage versus gas pressure.

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Figure 1 shows dependence of the arc discharge voltage on admitted gases pressure during operation with a titanium cathode.

Increase of the discharge voltage under pressure increase of chemically active gases is typical for this process. As the pressure increases the discharge voltage decreases. It is caused by less diffusion of the cathode material vapors and lower energy dissipation from the discharge zone, which facilitates burning of the arc. For heavier gases this decrease is faster.

For chemically active gases the voltage reduction is preconditioned by thin oxide or nitride film formation on the cathode, which reduces a threshold arc current and facilitates initiation of a cathode spot. Mechanism of the discharge voltage increase in the right part of the diagram is more complicated. As far as the chamber dimensions are rather significant, metal vapor pressure is sharply reduced as the distance from the cathode is increased and interaction of plasma with the gas target becomes essential. For most of the gases at relatively low electron energies the ionization process goes step by step. Monatomic gases argon and helium are exceptions.

It is known [3] that interaction of titanium ions with nitrogen molecules and charge exchange of double-charged titanium ions are a source of molecular ions formation, in particular nitrogenous.

Figure 2 shows dependence of discharge voltage on pressure for carbon dioxide, pure oxygen, air and mixture of oxygen with helium.

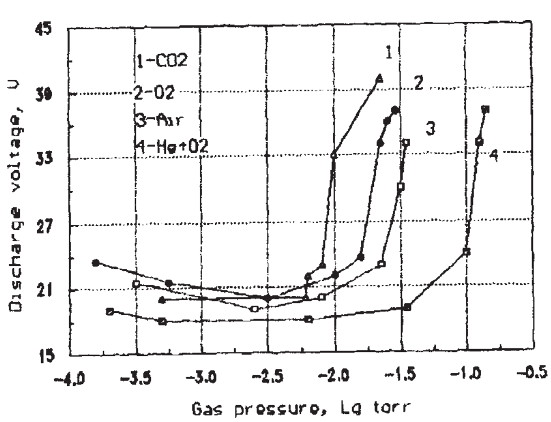


Figure 2. Discharge voltage versus gas pressure.

As oxygen partial pressure is decreased the curves are displaced in the direction of larger total pressure. However for carbon dioxide the voltage growth is observed under pressure, lower than that for oxygen.

Admittance of various gases changes the character of cathode spots migration essentially.

Theoretically as gas pressure is increased the speed of the cathode spots migration grows up to a certain critical pressure, then it is reduced, the spot stops and the speed is reversed [1].

However, in real vacuum deposition machines such conditions are practically not realized.

Data of plasma emissive spectroscopy show that admittance of various gases results in the intensification of emission lines not only of these gases but also of titanium. Figures 3-4 show intensity of titanium line in the case of argon and nitrogen admittance. Variation of the lines is caused by two reasons.

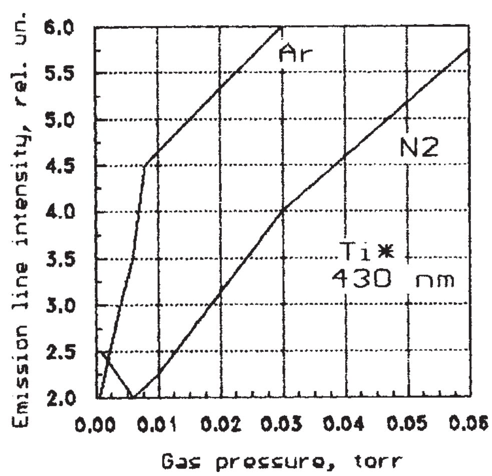
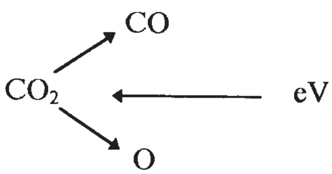


Figure 3. Emission line intensity versus gas pressure.

First, under the speed increase of the cathode spots migration content of the droplet phase is sharply reduced and atomic titanium content is increased. Secondly, under increase of molecular gases pressure content of multiple-charged titanium ions is reduced and content of exited titanium atoms is increased at the expense of dissociation and ionization of reactive gas molecules. Dissociation and ionization of molecules at the expense of discharge exchange of titanium ions determines the discharge voltage increase under increased pressure. It is also proved by intensification of atomic nitrogen line under increase of the arc discharge current (Figure 5).

In the case of carbon dioxide admittance into the discharge gap the molecule is dissociated according to the scheme:



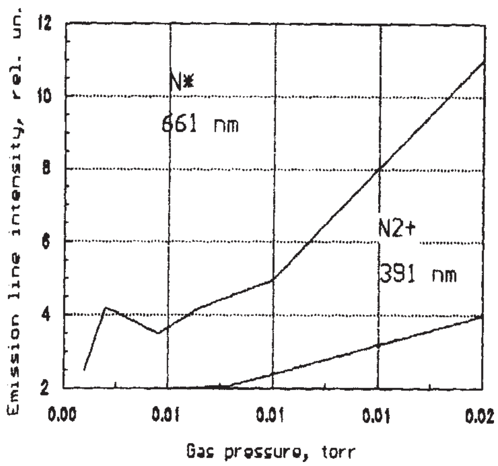


Figure 4. Emission line intensity versus gas pressure.

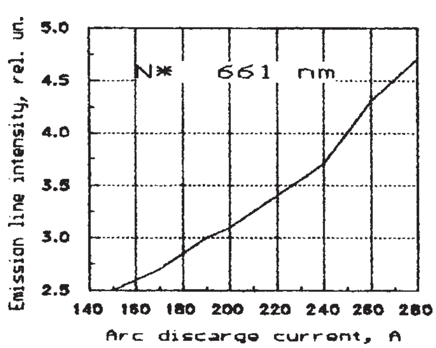


Figure 5. Emission line versus arc discharge current.

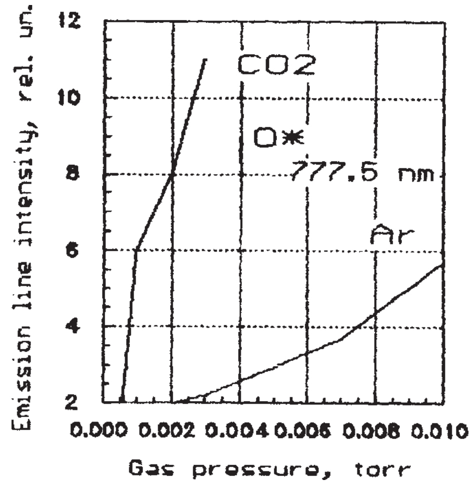


Figure 6. Emission line intensity versus gas pressure. 1 - CO_2 inlet; 2 - air inlet.

Figure 6 shows the dependence of atomic oxygen lines on argon and carbon dioxide pressure. It is typical that the dissociation of the carbon oxide molecule does not occur because of high bond energy in this molecule.

In the case of admittance of acetylene or its mixture with argon into the discharge gap the titanium line intensity is reduced.

Gas pressure and character of titanium ions interaction with the gas target determine also mechanical properties of the deposited coatings. It is known [4, 5] that bombardment of the growing film with high-energy neutral atoms of metals results in the development of high internal compressive stresses in the film. Gas pressure increase reduces energy of metal atoms and stresses in the film. Figure 7 shows dependence of internal stresses in the titanium nitride film on the gas pressure.

As it is visible compressive stress value is reduced as the pressure grows and sign reversal of the stresses (conversion of compressive stresses into tensile stresses) is observed at pressure $7.5*10^{-3}$ torr. Value of compressive stresses under pressure $9*10^{-4}$ torr reaches 1200-1800 kg/mm². Behavior of the curve does not practically depend on admitted gas. It can be either nitrogen or mixture of nitrogen with argon or helium. It is thus possible to adjust mechanical properties of titanium nitride films in a wide range without changing

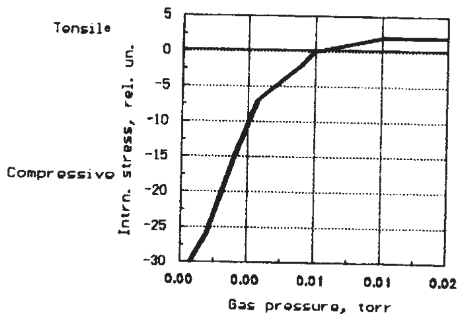


Figure 7. Internal stresses of TiN film versus gas pressure.

its stoichiometric structure on account of the inert gas not participating in the reaction but acting as ballast.

On the basis of received results a number of technological processes have been developed to be used in industrial equipment [6].

First, deposition of titanium nitride films onto heat sensitive substrates (individual plastic parts, polymeric films, lacquered metal), glass and ceramics without preliminary heating of the substrate. The coatings are used for decorative purposes, as conducting corrosion resistant layer and sun-protective layer (on glass). Temperature of the substrate does not exceed 30-40 °C. Operation at total pressure (5-9)*10^{-3} torr in the atmosphere of nitrogen and argon or helium makes it possible to deposit high adhesive coatings with droplet dimensions no more than 5 µm, without deteriorating optical properties of the films. The deposition of multi-layer coatings with smooth decrease of argon pressure enables to increase hardness of outside layers. Coating thickness can reach 0.5 µm. Appearance of the deposited coatings does not differ from that of the magnetron deposited films. Electrical resistivity of such films makes 25 µohm*cm, that is much lower than in case of other deposition methods.

Secondly, formation of oxide films on cold surfaces of plastics, glass and metal, utilizing carbon dioxide as reactive gas. Only one oxygen atom is removed in CO_o discharge. It enters into reaction with titanium, forming titanium oxide. Carbon oxide, not splitted further due to high bond energy, partially is pumped out by the vacuum pumps and partially is reduced to dioxide in contact with oxidized heated surface of the cathode in the area of a cathode spot. Such oxidation reduction process on the cathode allows to operate in a wide range of pressure, down to 8*10^{-3} torr, and to deposit the layers with different properties in comparison with utilization of oxygen as reactive gas, when there is complete poisoning of the cathode already under pressure 3*10^{-3}.

Arc vaporization of titanium in the medium of carbon dioxide allows to deposit interference colored films on cold surfaces of plastics, glass and metal, and blank transparent films with transmissivity in visible area 85 %, providing blooming of multi-layer coatings. So, two-layer titanium nitride - titanium oxide film allows to increase transparency of initial nitride film on 10-15 %. Carbon dioxide utilization instead of oxygen much improves operation of the pumping system and improves the safety engineering.

Thirdly, carbon layers deposition by arc vaporization of titanium in the medium of acetylene and mixture of acetylene and argon. In this process it is possible to deposit a soft conductive film of black color with low factor of friction, a black decorative film and slightly colored transparent film with high insulating properties, close to diamondlike layers. Properties of the films vary at the expense of changes both of total pressure and ratio of acetylene and argon.

CONCLUSION

Usage of the possibilities to adjust pressure and composition of gas medium in arc discharge allows to expand a range of properties of the deposited films and to realize the processes in industrial scale under minimum expenses.

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