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Properties of Surface Layers Produced from a Metalorganic Titanium Compound Under Glow Discharge Conditions

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Abstract. A prospective line in the development of thermo-chemical treatments under glow discharge conditions is to work out new techniques of producing multicomponent layers, e.g., composite layers, by combining various treatments, such as e.g. plasma nitriding and the PACVD method. The combined properties, appropriately selected and complementary to one another, of the single-component layers obtained using one of these processes, permit widening the application range of the layers. The paper specifies the conditions under which the multicomponent layers of Ti(OCN) type and composite layers of the nitrided + TiN or nitrided + Ti(OCN) type can be produced on steel. The structure and properties of the layers thus obtained are also described.

1. INTRODUCTION

The prospects of the further development of surface engineering lie in new low-temperature CVD techniques for the deposition of hard surface layers, such as e.g. the glow discharge assisted- or pulse plasma CVD methods [1-3]. In the CVD technique carried out under glow discharge conditions (the PACVD process), the gaseous medium is activated not only thermally (apparatus with the hot-anode [3]), but also electrically. This permits a considerable reduction of the deposition temperature. In the present work, TiCl₄, commonly used for producing TiC, TiN, Ti(CN) layers by CVD processes, was replaced by a mixture that contained tetraisopropoxytitanium vapours - Ti(OiC₃H₇)₄, hydrogen and nitrogen. Because titanium, oxygen and carbon are present in the Ti(OiC₃H₇)₄ compound, the layer produced contains these elements and in addition nitrogen from the gas mixture [2,4]. The layer may be described as Ti(OCN). Such layers, showing a good resistance to wear, have already been obtained using the gaseous atmosphere composed of TiCl₄, N₂, CH₄ and CO₂ [5].

2. EXPERIMENTAL METHODS

The multicomponent layers of the Ti(OCN) type and composite layers built of a nitrided layer covered with a Ti(OCN) or TiN layer were produced in a universal apparatus designed for glow discharge assisted thermo-chemical treatments. The apparatus permits plasma diffusion processes (e.g., nitriding, carbonitriding, boriding) and PACVD processes to be carried out in various gaseous atmospheres. It also enables the composition of the gaseous mixture to be modified during the process [3]. A schematic diagram of the apparatus is shown in Fig. 1.

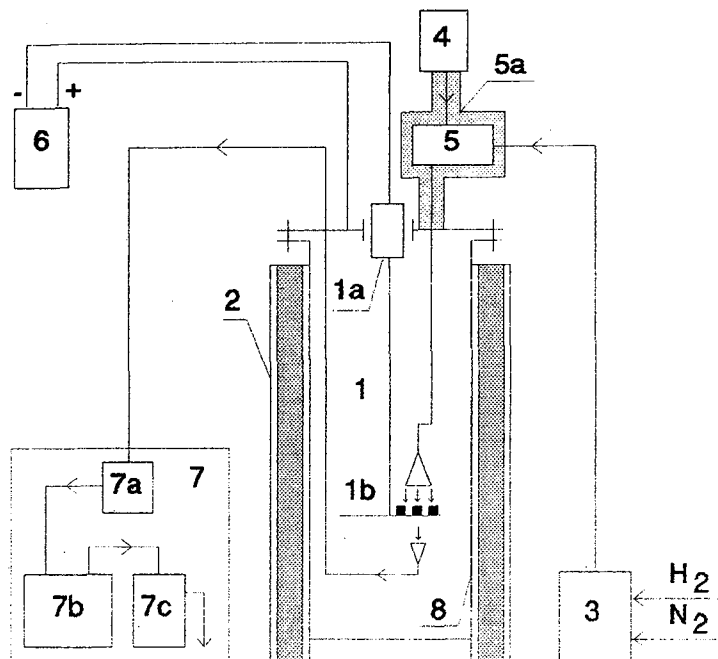


Figure 1. Schematic diagram of the apparatus for thermo-chemical treatments carried out under glow discharge conditions: 1 - reaction chamber with an electric bushing (1a) and a treated part holder (1b - the cathode), 2 - resistance furnace, 3 - dosing device, 4 - $\text{Ti}(\text{O}i\text{C}_3\text{H}_7)_4$ or TiCl_4 dosing device, 5 - $\text{Ti}(\text{O}i\text{C}_3\text{H}_7)_4$ vapours + H_2 + N_2 mixer (5a - thermostat), 6 - dc voltage supply unit, 7 - vacuum system (7a - cooling trap, 7b - vacuum pump, 7c - an absorber of gases), 8 - reaction chamber (the anode).

The composite layers were produced by the so-called single stage processes, in which after the plasma nitriding in the $\text{N}_2 + \text{H}_2$ atmosphere, TiCl_4 or $\text{Ti}(\text{O}i\text{C}_3\text{H}_7)_4$ vapours mixed with $\text{N}_2 + \text{H}_2$ were introduced into the reaction chamber and, by changing the current-voltage parameters, TiN or $\text{Ti}(\text{OCN})$ layers are produced. The nitriding process lasted 3 hours and after that, a multicomponent layer was obtained using a voltage of 1100V, a total pressure of 5 hPa., a coating time of 2 hours. The optimum temperature for producing $\text{Ti}(\text{OCN})$ layers was 500°C [6]. The multicomponent and composite layers were formed on Armco iron (0.05%C), 1H18N9T steel (0.1%C, 18%Cr, 9%Ni, 0.5%Ti) and SW7M steel (0.88%C, 4.3%Cr, 5%Mo, 6.5%W, 1.95%V). The stainless steel of the 1H18N9T type was nitrided under glow discharge conditions at a temperature of 760°C and then TiN layers were produced at 650°C or $\text{Ti}(\text{OCN})$ layers at 500°C. The content of TiCl_4 or $\text{Ti}(\text{O}i\text{C}_3\text{H}_7)_4$ vapours in the gas atmosphere was about 10% (by volume). The metallographic microsections were etched either with nital (SW7M steel and Armco iron) or with an etchant based on HNO_3 , HF and H_2O (1H18N9T steel specimens). The resistance to corrosion of the layers were examined by the potentiodynamic method. The measurements were made in a 0.5M NaCl aqueous solution at a temperature of 25°C. The reference electrode was a saturated calomel electrode. The electric potential was varied at a rate of 1000mV/h. The potentiostat used was a Taccusel PRT-20 [3,4]. The resistance to frictional wear was examined using the "three rollers + taper" method under the following conditions: the unit load - 200, 400MPa, the friction rate - 0.58m/s, the lubricant medium - the Lux 10 lubricant, drip-fed at a rate of 30 drops/min, the wear depth - measured microscopically, the frictional load - increased at 10min intervals [7]. In this test friction is applied between three 8mm-diam. cylindrical specimens (rollers) and a rotating conical counterspecimen (a taper). The linear wear, expressed as the wear depth was determined by measuring the diameters of the ellipses formed on the surface layer of the individual rollers. The counterspecimen was made of AISI45 steel, quench hardened and tempered to a hardness of 30HRC. The test time was 100 min, but it was interrupted at intervals of 10 min at which the worn area (elliptical in shape) was measured. After each interruption the load was increased so as to maintain a constant unit load.

3. RESULTS

Fig. 2 shows an example of microstructures of the Ti(OCN) layers and of the composite layers of the two types: nitrided + TiN and nitrided + Ti(OCN), formed on various steels. The TiN or Ti(OCN) layers were up to $10\mu\text{m}$ thick and their surface hardness was in the range from 1500 to 2150 HV 0.05.

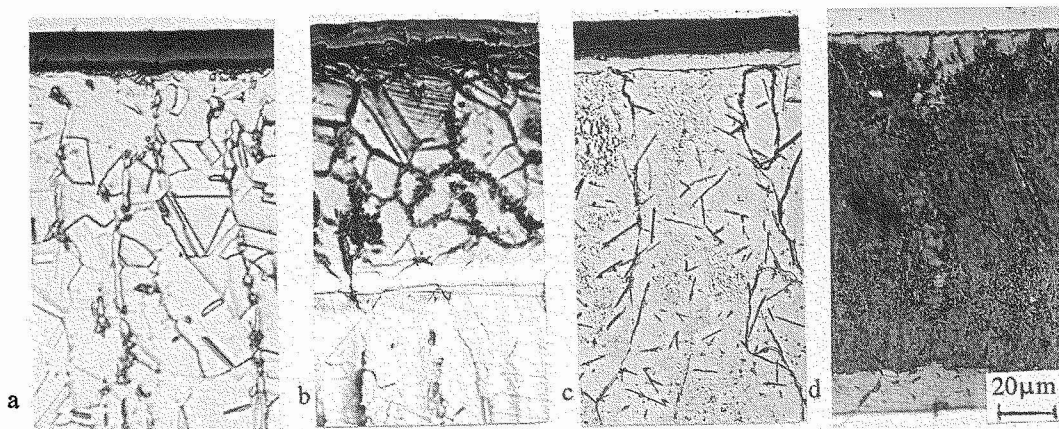


Figure 2. Microstructures of a multicomponent and composite surface layers formed on various steel grades: a) Ti(OCN) on 1H18N9T steel, b) composite nitrided + Ti(OCN) layers formed on 1H18N9T steel c) Ti(OCN) on Armco iron and d) composite nitrided + TiN layer on 1H18N9T steel.

Fig. 3a,b compare the potentiodynamic curves representing the corrosion resistances of Ti(OCN) and of composite layers (both the nitrided + TiN and nitrided + Ti(OCN) types) with the curves representing the corrosion resistances of the substrate material and of a nitrided layer.

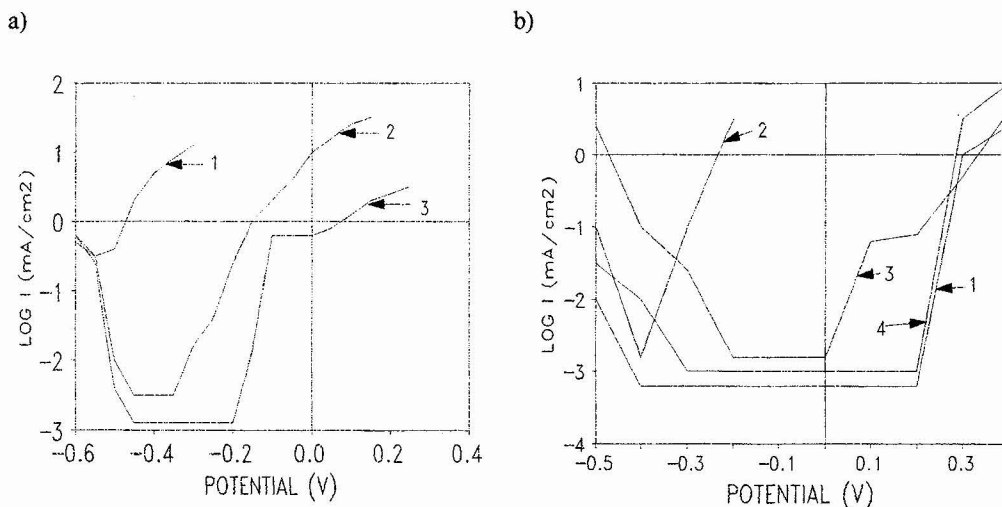


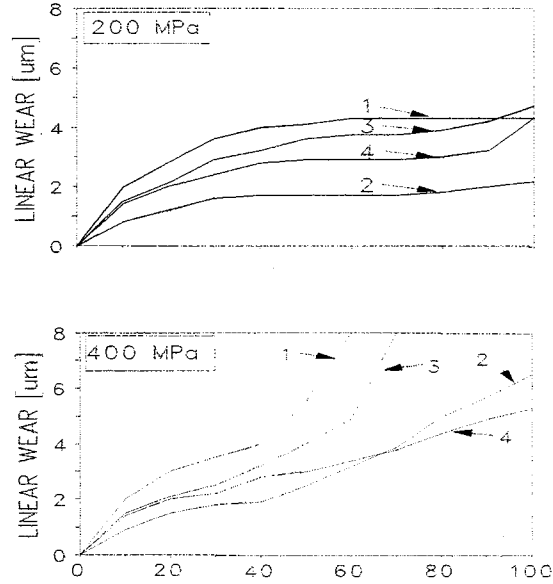
Figure 3. Anodic polarization curves measured in a 0.5M NaCl aqueous solution for:

a) Armco iron (1), Ti(OCN) layer (2), composite nitrided + Ti(OCN) layer (3) on Armco iron

b) 1H18N9T steel (1), nitrided layer (2), composite nitrided + Ti(OCN) layer (3), composite nitrided + TiN layer (4) on 1H18N9T steel.

Figure 4 shows the resistance to frictional wear of the surface layers formed on 1H18N9T and SW7M steels.

a)



b)

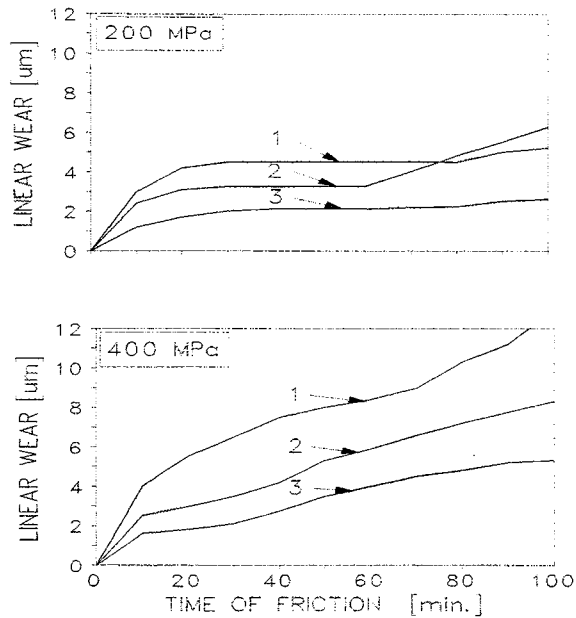


Figure 4. Linear wear occurring on a) 1H18N9T steel: a nitrided layer (1), a composite nitrided + TiN layer (2), a Ti(OCN) layer (3), and a nitrided + Ti(OCN) layer (4); and b) on SW7M steel: a Ti(OCN) layer (1), a composite nitrided + Ti(OCN) layer (2), a composite nitrided + TiN layer (3) as a function of friction time at unit loads 200 and 400 MPa.

Our investigation have shown that the composite layers of the nitrided + TiN or nitrided + Ti(OCN) layer type produced on both Armco iron and stainless or high-speed steel guarantee an increase of the corrosion resistance (Fig. 3) and the frictional wear resistance (Fig. 4). It is known that the corrosion resistance of surface TiN layers depends on their porosity and structural defects [8,9], and that the nitriding of the stainless steel lowers markedly its corrosion resistance. The increased corrosion resistance of the composite layers can be explained by the fact that factors such as the temperature and chemical composition of the gaseous atmosphere, the electrical activation of the gaseous medium, the highly developed surface zone of the nitrided layer and the structural defects produced in it by cathode sputtering, and also the possibility of producing a nitrided layer without a compounds zone, permit us to control the microstructure and chemical composition and thereby the corrosion properties of the TiN or Ti(OCN) layers produced. When analysing the anodic polarization curves we can see that the composite layers of the nitrided + Ti(OCN) type produced for example on Armco iron increase the corrosion potential from about -600mV in the case of uncovered (without a surface layer) Armco iron or from -350mV for a Ti(OCN) layer to -200mV obtained for composite layers of the nitrided + Ti(OCN) type. Moreover, we can see that the layers have undergone passivation. This guarantees a improvement of the corrosion resistance. The nitriding process applied to stainless steel worsens its resistance to corrosion (the corrosion potential is -500mV), whereas the deposition of, for example, a surface TiN layer on prenitrided steel decidedly improves the corrosion resistance of the composite layer thus obtained so that is not worse than that of stainless steel. This is due to the very fine-grained structure of the titanium nitride produced. The results of the examination of the resistance to frictional wear have shown that a nitrided layer increases this resistance since it provides a sufficiently hard support for the Ti(OCN) or TiN layer. We can see from Fig. 4a that by producing composite layers of the nitrided + Ti(OCN) or nitrided + TiN type (diffusion nitrided layers deposited for example on stainless steel have a thickness in the range 60 to 120 μ m depend on the conditions of prenitriding process and a hardness about 1200 HV0.05) we can markedly increase the wear resistance even, though the hardness of the core material (stainless steel) is low. This is best observed when the wear examinations are carried out at high unit loads (400 MPa.), at which the stainless steel specimens covered with a nitrided layer or with a Ti(OCN) layer alone undergo seizure (Fig. 4a).

4. FINAL REMARKS

The multicomponent layers of the Ti(OCN) type and the composite layers of the nitrided + TiN or Ti(OCN) layer type show a good resistance to corrosion and to frictional wear. Under glow discharge conditions, these layers can be produced at a temperature between 500 and 550°C. Pre-nitriding of the steel substrate increases the resistance to corrosion and to frictional wear, so that the layers may be used for practical purposes. An important advantage of the process lies in that the atmosphere does not contain chlorine.

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