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Formation and properties of composite layers on stainless steel

T. WIERZCHON, J. MICHALSKI, J. RUDNICKI
Institute of Materials Science and Engineering, Warsaw University of Technology, 02-524 Warszawa ul. Navbutta 85, Poland
B. KUŁAKOWSKA, W. ŻYRNICKI
Institute of Inorganic Chemistry and Metallurgy of Rare Elements, Technical University of Wrocław, 50-370 Wrocław ul. Wybrzeże Wyspianskiego 27, Poland

By applying glow discharge in a gaseous mixture composed of $TiCl_4$–H_2–N_2 it is possible to produce TiN layers or – if the process is conducted in two stages differing in the atmospheres used – composite layers, e.g. a nitrided layer covered by a titanium nitride layer. Electric activation of the gaseous medium and of the surface under treatment make it possible to reduce the treatment temperature down to 550 °C. This paper presents a description of the installation for producing composite layers, made of a nitrided sublayer, and a surface TiN layer on steels, as well as the results of structural examinations, wear and corrosion tests performed on the layers and qualitative analysis of $TiCl_4$–H_2–N_2 plasma.

1. Introduction

With the increasing progress in engineering, a growing need has been felt for materials that show improved mechanical properties, such as an increased resistance to corrosion, erosion, and high temperatures. This need may be met by making use of the advances made by surface engineering, i.e., in producing layers of desired structure (properties) on the surface, of a part under treatment. New methods for producing surface composite layers combining the known nitriding and titanizing by glow discharge [1–4] or boriding and nitriding [5] processes seem to have the most prospects. The combined properties, appropriately selected and complementary to one another, of the single layers obtained by the individual processes, permit widening the application range of the layers. For example, the plasma nitriding process usually decreases the resistance to corrosion of stainless steels but increases their resistance to frictional wear [6]. If we, in addition, produce a titanium nitride layer on the surface of the nitrided steel, the resistance to corrosion appropriate for steel is preserved, whereas the resistance to friction increases [2, 7].

2. Experimental procedure

The apparatus used for producing the composite layers that contain a nitrided layer and a TiN layer at its surface is shown diagramatically in Fig. 1.

The layers were produced using either a single step process, in which, after glow discharge nitriding in an $N_2 + H_2$ atmosphere, $TiCl_4$ vapours were introduced into the atmosphere and titanizing was carried out at different current–voltage parameters, or they were produced in two phase processes, i.e., the layers produced by nitriding were first examined and, then, subjected to titanizing in a hot anode apparatus used for glow discharge treatment [1, 2]. The specimens were made of 1H18N9T steel (18% Cr, 9% Ni, 0.5% Ti, 0.1% C). The glow discharge nitriding was performed at 680, 780 and 880 °C. By way of example, Fig. 2 shows the microstructure of some nitrided layers thus obtained. We can see from Fig. 2 that the layers produced at 780 °C were the thickest and their structure was more complicated than that of the other layers. The metallographic microsections were etched electrolytically at a voltage of 6 V and a current density of 0.2 mA cm^{-2}, using an etchant based on oxalic acid. Then, the nitrided specimens were subjected to titanizing by glow discharge at temperatures of 680, 780 and 880 °C. Similar composite layers were also obtained on other steel grades, such as SW18 high speed steel (0.7–0.85% C, 3.8–4.8% Cr, 16.5–19.5% W, 1–1.5% V), NC4 tool steel (0.95–1.4% C, 1.3–1.65% Cr, 0.2–0.4% Mn) and 36H3M steel (0.32% C, 0.4% Mn, 2.8% Cr, 0.5% Mo), using the two step method at various temperatures. The structures of the nitrided and composite layers were examined metallographically by observing the cross-sections of the specimens after they have been halved and clamped in metallographic holders.

The wear resistance was measured by a "three-rollers" friction test [8, 9]. In this test, friction is applied, under specified conditions, between three, fixed, 8 mm diameter, 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 surfaces of the individual rollers. The results were then averaged. The counterspecimen was

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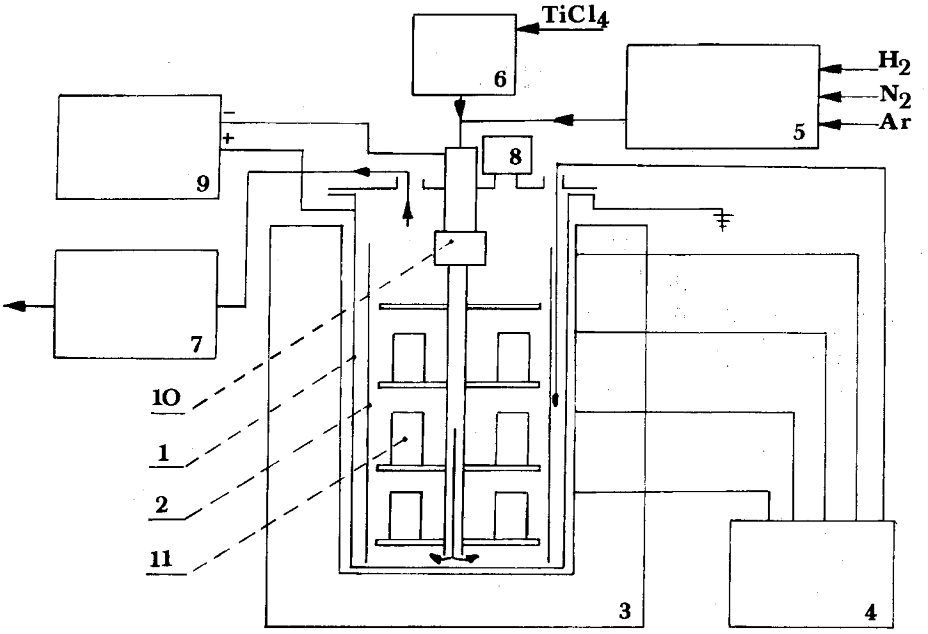

Figure 1 Block diagram of the hot anode apparatus for conducting PACVD processes: (1) reaction chamber; (2) inner shield; (3) resistance furnace; (4) temperature stabilization and recording system; (5) gas dosing device; (6) $TiCl_4$ vapours dosing device; (7) vacuum system; (8) pressure gauge; (9) voltage feeder; (10) current inlet device; (11) treated part.

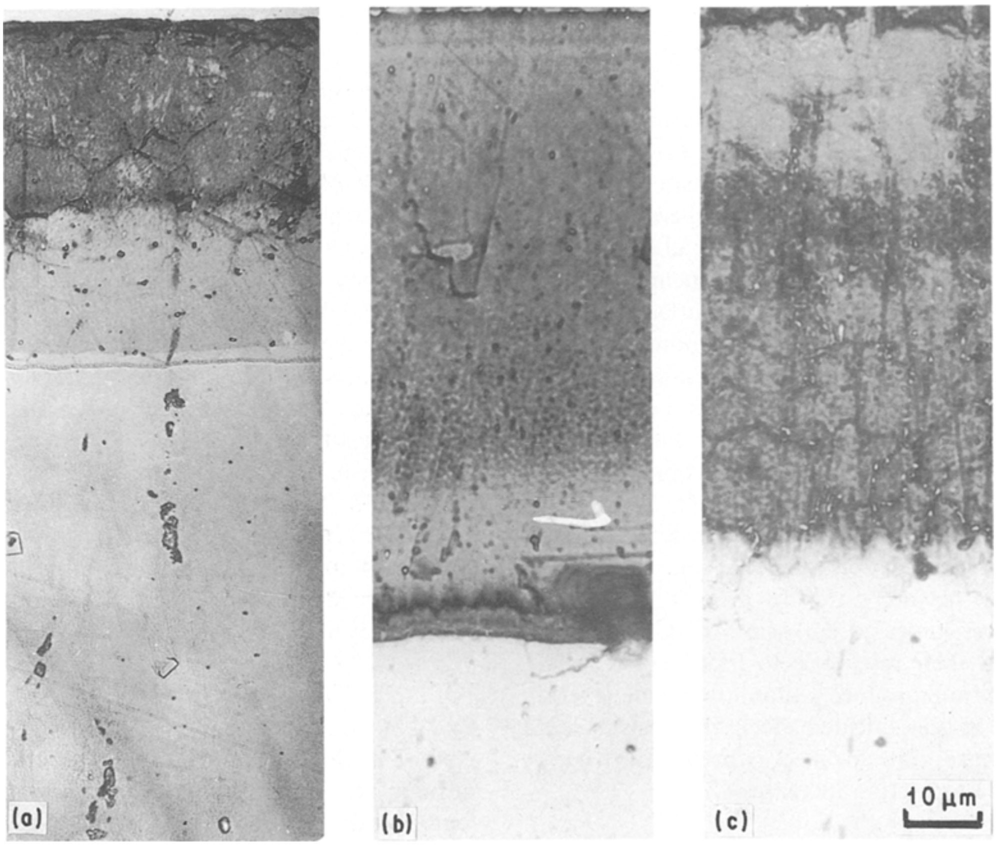

Figure 2 Microstructures of the nitrided layers produced under glow discharge conditions. The process parameters were: (a) $T = 680\,^{\circ}C$, $t = 9$ h, P = 6.7 hPa; (b) $T = 780\,^{\circ}C$, $t = 9$ h, P = 6.7 hPa; (c) $T = 880\,^{\circ}C$, $t = 9$ h, P = 6.7 hPa ($N_2 + H_2$).

made of AISI45 steel, quench hardened and tempered to a hardness of 30 HRC. The test lasted for 100 min, but it was interrupted at intervals of 10 min, at which the worn area was measured. After each interruption, the load was increased to compensate for the increased worn area so as to maintain a constant unit pressure of 100, 200, 300 and 400 MPa. The maximum pressure drop observed during the test was 10%.

The tribological properties of austenitic stainless steel nitrided at 780 °C and of the composite nitrided + TiN layers produced at 780 and 680 °C were examined and compared.

The specimens were also examined by X-ray techniques, using a Philips X-ray diffractometer with CoK_α radiation, and by scanning electron microscopy methods using a Tesla BS 300 microscope.

The nitrided stainless steel specimens and the composite layers deposited on 1H18N9T steel were subjected to corrosion tests in a non-aerated 0.5 M NaCl water solution. The corrosion resistance of these specimens was estimated from the anodic polarization potentiodynamic curves recorded at an advance rate of 1000 mV h^{-1}. Each polarization curve represented the mean of the values obtained for three specimens.

A qualitative analysis of the $TiCl_4$–H_2–N_2 plasma (the cathode made of Armco iron) was performed on specimens prepared with and without the ion pre-nitriding of the cathode (in the latter case the cathode is referred to as the clean cathode). The analysis made use of the spectroscopic method [10], by recording the spectrum of the plasma that glows within the entire space between the cathode and the steel anode spaced at about 10 mm. The spectrographs were taken with a plane grating PGS-2 spectrograph using Kodak plates. The Armco cathode was nitrided at 500 °C for 3 h, and then after 15 min from the moment when $TiCl_4$ vapours were passed into the discharge region, the recording of the plasma spectrum was started. The spectrographs were taken within a wide spectral range, from 200–700 nm.

3. Results

Fig. 3 shows the microstructure of the composite layers produced on 1H18N9T steel under glow discharge conditions. The layers, especially those produced at 780 °C, were relatively thick, in a uniform way, and their surface hardness was about 2000 HV 0.05. By comparing the structures of the nitrided layers obtained at 880 °C (Figs 2 and 3) we can see that during the titanizing process the nitride phases precipitate and coagulate at grain boundaries (Fig. 3c). Moreover, the surface of the TiN layer produced at 880 °C is much more developed and its thickness is non-uniform. A comparison of Figs 2 and 3 suggests that the reduced thickness of the nitrided layer observed after the formation of the TiN layer may be due to the diffusion of nitrogen from the nitrided layer into the region where the TiN layer is being formed. By comparing the mechanisms of the formation of a TiN layer on 1H18N9T steel after and before the steel is nitrided, we find that the nitrided layer acts as a catalyst for the formation of the TiN layer. With other process parameters unchanged, the TiN layer obtained in the former case had a thickness of about 8 μm whereas that produced in the latter case was only about 3–4 μm thick (Fig. 4). A phase analysis has shown that specimens made of nitrided and titanized steel contain a surface titanium nitride layer (Table I).

Fig. 5 shows the results of comparative friction wear tests on composite layers produced at: (b) 780 and (c) 680 °C on 1H18N9T steel and layers only subjected to nitriding at (a) 780 °C. The wear is plotted as a function of time at a constant surface pressure of 100, 200, 300 and 400 MPa. We can see from Fig. 5 that the wear resistance of the composite layers is greater than that of the nitrided layers.

Fig. 6 shows the structures of composite layers of the nitrided layer plus the TiN layer type produced on various grades of steel. Fig. 7 shows the surfaces of the specimens subjected to the corrosion tests, and the anodic polarization curves for the nitrided layers and composite (nitrided plus a surface TiN film) layers. It follows from Fig. 7 that the corrosion resistance of the composite layers depends on the surface structure of the TiN layer. If the TiN layer produced has a fine

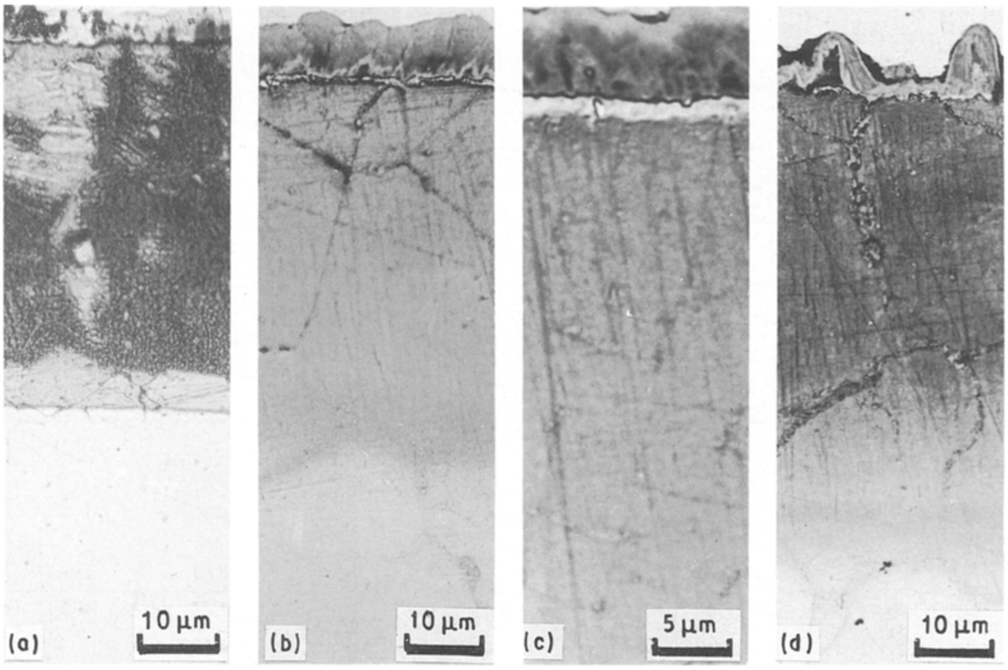

Figure 3 Microstructures of the composite layers of the nitrided layer + TiN type produced on 1H18N9T steel at: (a) 680; (b) 780 and (c) 880 °C.

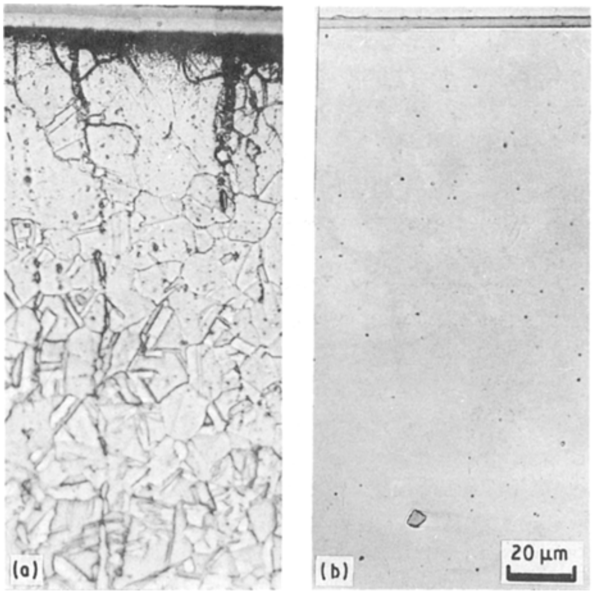

Figure 4 TiN layer produced on: (a) pre-nitrided 1H18N9T steel and (b) the same steel not subjected to nitriding, $T = 680\,^{\circ}\mathrm{C}$.

TABLE I The structure of 1H18N9T steel after plasma-nitriding and titanizing

Treatment temperature (°C)	Identified phases
780 (nitriding alone)	γ' ($\mathrm{Fe_4N}$), CrN, Feα, Feγ
680 (nitriding + 780°C titanizing)	TiN, Feα, Feγ (TiN layer thickness $\geqslant 10\ \mu$m)
780 (nitriding + 680 °C titanizing)	TiN, ε ($\mathrm{Fe_2N{-}Fe_3N}$) Feα, CrN (TiN layer thickness $< 5\ \mu$m)

grained structure (1), the corrosion resistance is high: the corrosion potential is $+180$ mV. In specimens with a nitrided layer the corrosion potential is -600 mV (3) and in those covered with a coarse grained composite layer, it is -500 mV (2). It follows from the spectrographs that, irrespective of whether or not the cathode surface has been pre-nitrided, the proportion of excited particles present in the $\mathrm{TiCl_4{-}H_2{-}N_2}$ plasma examined is similar. By way of example, Fig. 8 shows how the emission intensities of the active particles of a $\mathrm{TiCl_4{-}H_2{-}N_2}$ ($\mathrm{N_2{:}H_2} = 1{:}3$) plasma are distributed within the inter-electrode space. Within the range 280–500 nm, the spectrum was very intensive and contained many characteristic lines of titanium ions ($\mathrm{Ti^{II}}$) and atoms ($\mathrm{Ti^{I}}$), nitrogen ions ($\mathrm{N^{II}}$) and atoms ($\mathrm{N^{I}}$), hydrogen atoms, spectral bands of the $\mathrm{N_2^+}$ and $\mathrm{N_2}$ molecules, and the NH radical. Within the range 500–700 nm, numerous lines characteristic of the molecular spectrum of hydrogen were observed. Anyway, the spectra of the excited plasma differed significantly due to various concentrations of active particles, depending on whether the nitrided Armco iron cathode was used or the plasma was excited between the steel electrodes without the cathode pre-nitriding. As an example, Fig. 9 shows some fragments of the recorded spectra.

From an analysis of the results obtained, it has been found that in the plasma excited between the clean electrodes (without pre-nitriding), the emission intensity of nitrogen (in various forms – ions, radicals, etc.) was lower and the emission intensity of titanium ions ($\mathrm{Ti^{II}}$) and atoms ($\mathrm{Ti^{I}}$) was greater than their emission intensities in the plasma generated with the use of the pre-nitrided Armco cathode.

Thus our results indicate that in the presence of the pre-nitrided cathode the TiN layer grows more quickly [2] due to the greater concentration of active nitrogen particles. This may be, most probably, attributed to the cathode sputtering effect occurring under the

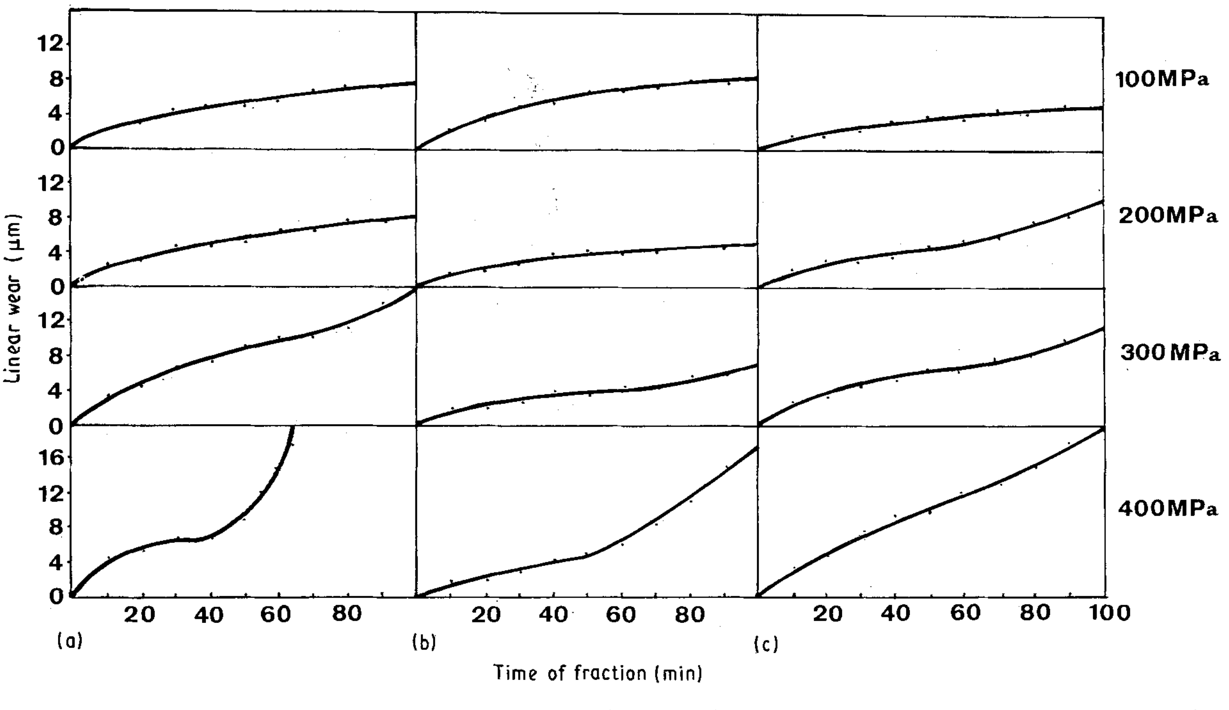

Figure 5 Linear wear of 1H18N9T austenitic stainless steel after: (a) nitriding, and of the same steel with a composite surface layer produced by nitriding and titanizing at (b) 780 and (c) 680 °C as a function of friction time at a constant surface pressure of 100, 200, 300 and 400 MPa.

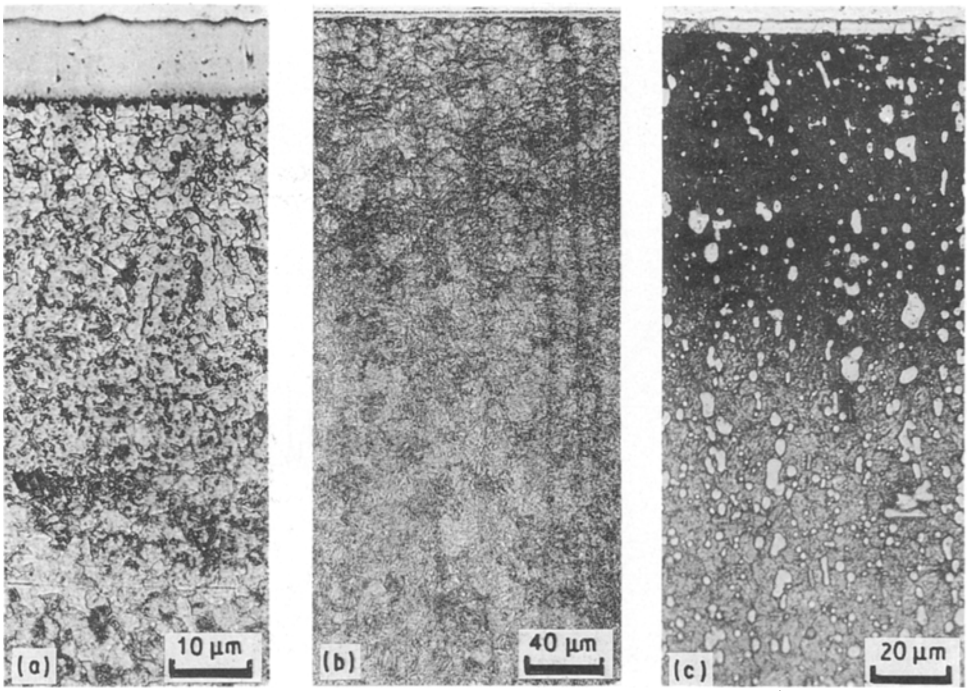

Figure 6 Microstructures of composite layers of the nitrided layer + TiN type produced on various steel grades: (a) NC4, $T = 850\,°C$; (b) 36H3M, $T = 550\,°C$; (c) SW18 $T = 550\,°C$.

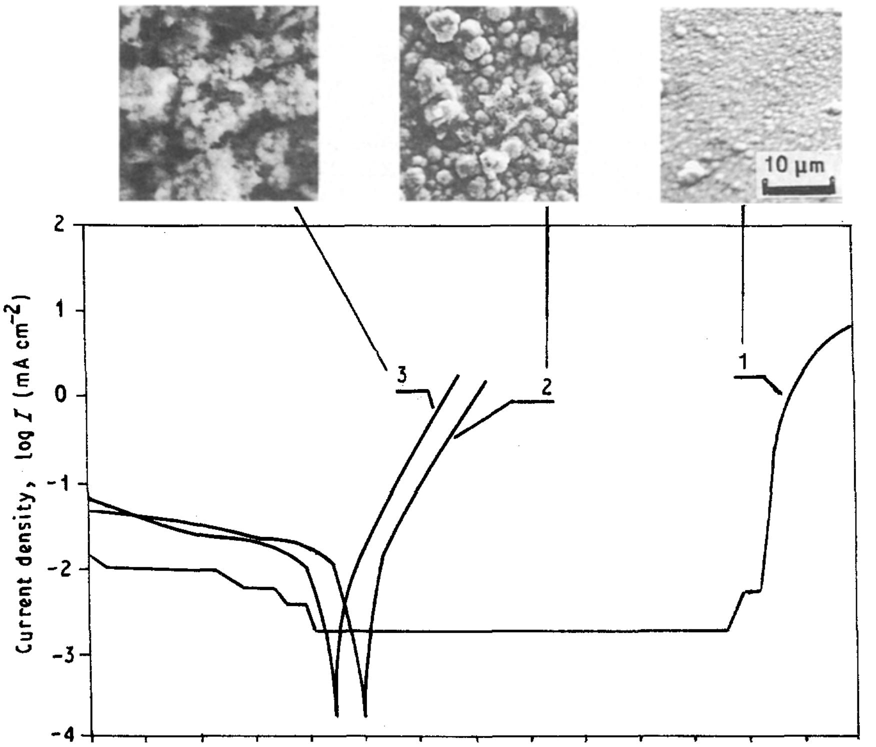

Figure 7 Microphotographs of the surface of 1H18N9T stainless steel specimens after: (3) nitriding and (1, 2) producing composite layers and the potentiodynamic curves of anodic polarization in a 0.5 M NaCl solution for these specimens.

conditions prevailing during this process [5,11]. This effect enhances the development of the treated surface and thereby increases the adhesion of TiN to the pre-nitrided steel substrate.

4. Conclusions

The results presented above show that under glow discharge conditions we can produce composite layers composed of a nitrided layer and a surface TiN layer, using either a single step process, i.e., a sole process during which the chemical composition of the gaseous atmosphere and the process parameters (the temperature and pressure) are changed, or a two step process involving glow discharge nitriding and titanizing performed separately. The composite layers obtained exhibit a high resistance to friction wear, a property

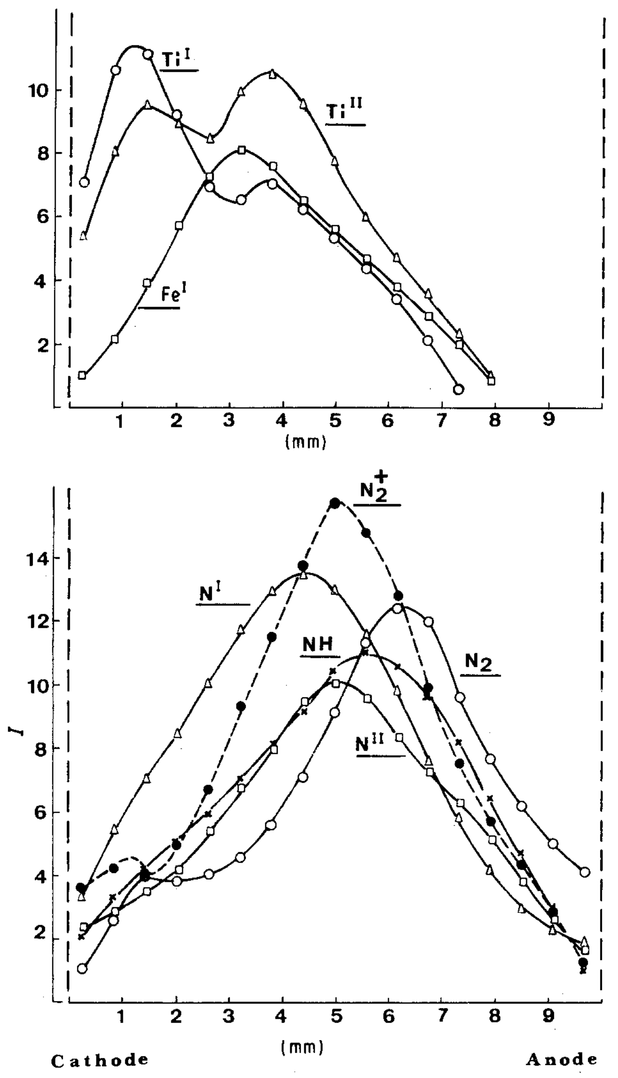

Figure 8 The emission intensity profile of the active particles within the inter-electrode space in a $TiCl_4$–H_2–N_2 mixture under glow discharge conditions.

which, in conjunction with the good anticorrosion characteristics of composite layers, widens the application range of stainless steels. Comparative examinations of the $TiCl_4$–H_2–N_2 plasma generated under glow discharge conditions have shown that titanium and nitrogen ions and atoms play an essential role in the formation of the TiN layer and this layer grows more quickly when a pre-nitrided steel substrate is used.

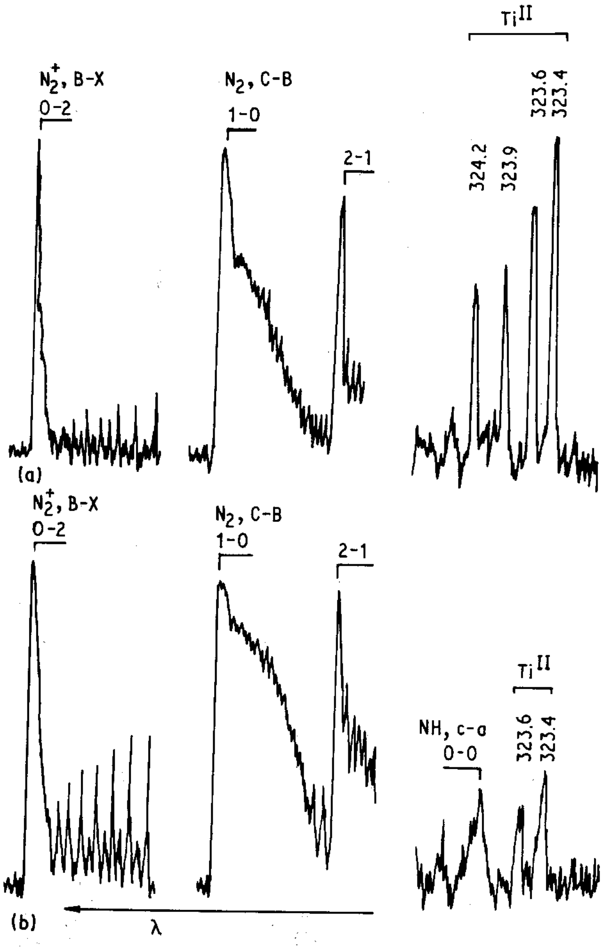

Figure 9 Spectra of the glow discharge plasma generated in a $TiCl_4$–H_2–N_2 (H_2:N_2 = 3:1) mixture: (a) without pre-nitriding of the cathode; (b) after the cathode has been pre-nitrided.

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