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Chemical vapour deposition of titanium nitride on plasma nitrided steel

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Ferritic and austenitic nitriding by the plasma nitriding technique were investigated for the modification of steel substrates prior to the chemical vapour deposition of titanium nitride at 1273 K. It was confirmed that prenitriding enhances the growth of the titanium nitride layer and it was found that a TiN coating can be formed using substrate derived nitrogen only. Control of porosity, arising during austenitic nitriding, was investigated and it was found that in practice this phenomenon could not be avoided.

1. Introduction

Thin hard layers of titanium carbide and nitride produced by chemical vapour deposition (CVD) have been used for a number of years as wear-resistant coatings on steel substrates. When titanium carbide is deposited directly on to carbon-containing steels at around 1273 K, the carbon in the coating material originates both from the gas stream and from the substrate [1–3]. The role of substrate-derived carbon is significant. Under the usual CVD process conditions for titanium carbide deposition on to steels, the substrate is often the main source of carbon and the gas-phase contribution of carbon is relatively small [2, 3]. This is particularly true in the case of plain carbon and low alloy steels and at short deposition times when the layer thickness is small. Indeed, titanium carbide can be deposited on steels without any carbon source in the gas phase and improvements in layer thickness can be brought about by precarburizing the substrate [1, 2].

Normally during the CVD of titanium nitride coatings, the nitrogen in the coating material is derived only from the reactive gas mixture. Nitriding of steels prior to CVD of titanium nitride has been reported, for example by Hänni and Hintermann [4], although the influence of substrate derived nitrogen on the CVD process in such cases is not clear. However, the modification of titanium carbide films and the formation of titanium nitride has been observed due to the outward diffusion of nitrogen from 304 stainless steel substrate on heating to 1000° C [5]. As a first approximation, it seems reasonable to presume that the deposition of titanium nitride on a nitrogen-rich steel surface at approximately 1273 K from titanium tetrachloride–hydrogen–nitrogen gas mixtures can be equated with the deposition of titanium carbide on iron–carbon alloys from titanium tetrachloride–hydrogen–methane gas mixtures at similar temperatures and that enhanced layer growth can be brought about by prenitriding the substrate.

2. Experimental procedure

Specimens of plain carbon steel (0.25% C) were plasma nitrided for 6 h at 823 K (ferritic nitriding) in an atmosphere of dissociated ammonia, nominally 25% N_2–75% H_2 and at 923 K (austenitic nitriding) for periods of up to 6 h in dissociated ammonia and mixtures varying from 15% N_2 to 3% N_2, the balance being H_2.

Chemical vapour deposition of titanium nitride was carried out in a hot-wall reactor at 1273 K. The reactive atmospheres used were, nominally, a 0.25 : 1 : 1 $TiCl_4:H_2:N_2$ gas mixture at 350 torr and a 1 : 175 $TiCl_4:H_2$ gas mixture at 660 torr. A 3 h reaction time was used with the nitrogen containing gas mixture and a 30 min reaction time was used with the nitrogen-free gas mixture. Both plain specimens and specimens nitrided for 6 h in dissociated ammonia at 823 and 923 K were used as substrates. Heat-up time to reaction temperature was approximately 1 h and was undertaken under a protective hydrogen atmosphere.

Specimens were sectioned and examined by optical metallography. The phases present in the surface zone were identified by X-ray diffractometry using copper radiation, with compositions confirmed by Auger electron spectroscopy in certain cases.

3. Results

Cross-sections of plain carbon steel nitrided in dissociated ammonia for 6 h at 823 and 923 K are shown in Figs 1 and 2, respectively. The surface layer in Fig. 1 was found by X-ray diffractometry to be composed of gamma prime iron nitride (γ'-Fe_4N). Needles of this nitride are also present in the subsurface zone. The dark etching case formed at the surface of the specimen in Fig. 2 was found to be composed of ferrite and gamma prime iron nitride which are the decomposition products of iron–nitrogen austenite [6]. The transformed zone is approximately 50 μm thick. Fig. 3 is the same section shown in Fig. 2 which has been prepared to illustrate the porosity present in the case. Cross-sections of specimens treated for 6 h at 923 K in

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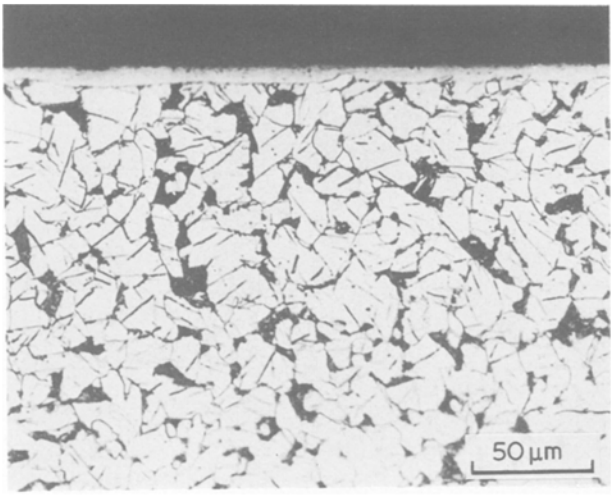

Figure 1 Plain carbon steel plasma nitrided in dissociated ammonia for 6 h at 823 K. Nital etch.

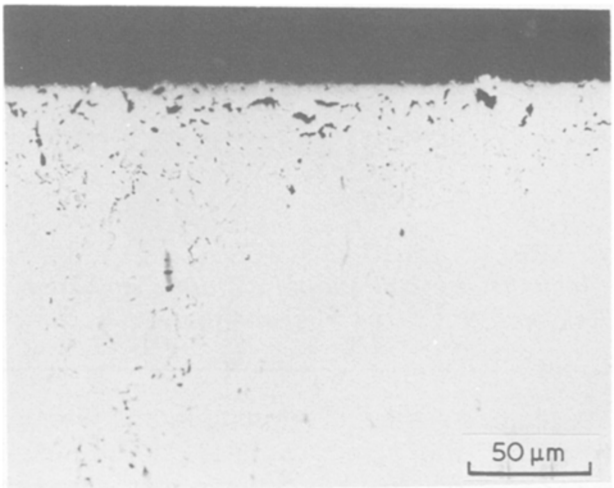

Figure 3 Plain carbon steel plasma nitrided in dissociated ammonia for 6 h at 923 K. Etched with nital and repolished to illustrate porosity in subsurface region.

5% N_2–95% H_2 and 3% N_2–97% H_2 glow discharges are shown in Figs 4 and 5, respectively. It is clear that austenite was formed during nitriding with the 5% N_2 glow discharge, but no transformed case is present after nitriding with 3% N_2. Indeed the latter treatment gives rise to decarburizing of the substrate as can clearly be seen in Fig. 5. Fig. 6 illustrates the case shown in fig. 4 which has been prepared to show up any porosity present. Porosity is clearly evident. A cross-section of a specimen after a 40 min treatment with a 25% N_2–75% H_2 glow discharge at 923 K is shown in Fig. 7. Some porosity is evident in the immediate subsurface of the steel, Fig. 8.

Fig. 9 illustrates the titanium nitride layer deposited on untreated steel and Figs 10 and 11 illustrate the titanium nitride layers deposited on ferritic nitrided and austenitic nitrided steel samples using the $TiCl_4$–H_2–N_2 gas mixture for 3 h. The layers on the pre-nitrided steels are of comparable thickness and are significantly thicker than the layer on the plain steel produced under the same CVD conditions. There is considerable porosity in the subsurface of the austenitic nitrided and coated specimen (Fig. 11), but such porosity does not occur in the ferritic nitrided and coated steel (Fig. 10). Fig. 12 illustrates the titanium nitride layer formed on the ferritic nitrided steel after 30 min in the nitrogen-free $TiCl_4$–H_2 gas mixture. In all cases the deposited layer was a yellow–gold colour and was confirmed by X-ray diffractometry to be titanium nitride. The lattice parameters determined were 0.4244, 0.4244 and 0.4241 nm for the ferritic nitrided, austenitic nitrided and untreated specimens, respectively. These values are in good agreement with the values of 0.4241 to 0.4249 nm reported in the literature [7] for pure near-stoichiometric titanium nitride. Auger electron spectroscopy, as shown in Fig. 13, revealed a very low level of carbon indicating a minimal contribution of substrate derived carbon to the growth of the coatings.

4. Discussion

The results of this study demonstrate that the formation of a titanium nitride coating by CVD can be markedly influenced by the presence of nitrogen in the substrate. The choice of a simple substrate probably accentuates the role of the substrate-derived nitrogen, because the presence of alloying elements in the substrate can be expected to influence the availability of nitrogen from the substrate. A titanium nitride coating can be produced on a steel surface in the

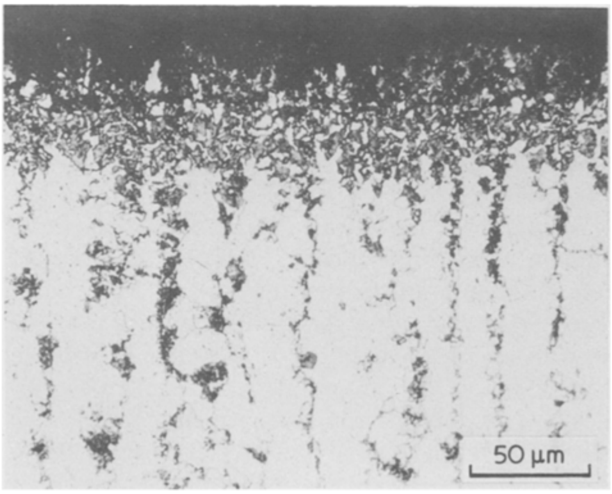

Figure 2 Plain carbon steel plasma nitrided in dissociated ammonia for 6 h at 923 K. Nital etch.

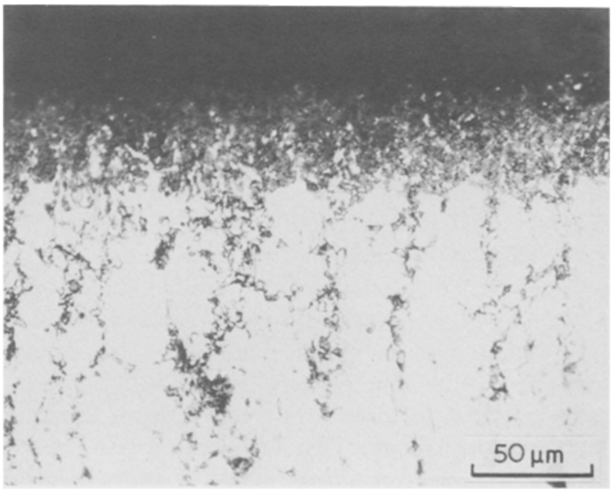

Figure 4 Plain carbon steel plasma nitrided in 5% N_2 to 95% H_2 for 6 h at 923 K. Nital etch.

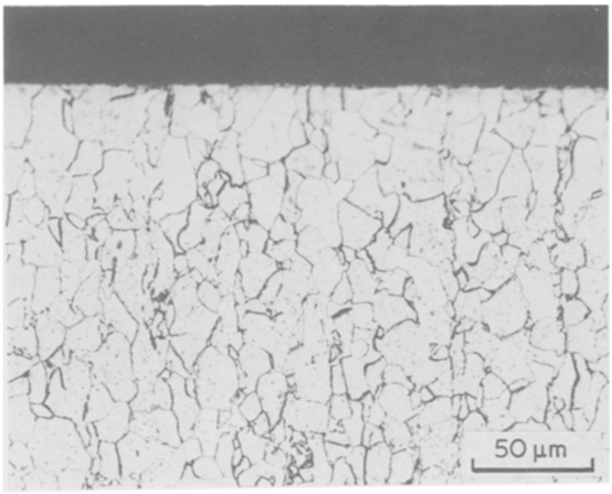

Figure 5 Plain carbon steel plasma nitrided in 3% N_2 to 97% H_2 for 6 h at 923 K. The surface region of the steel has decarburized. Nital etch.

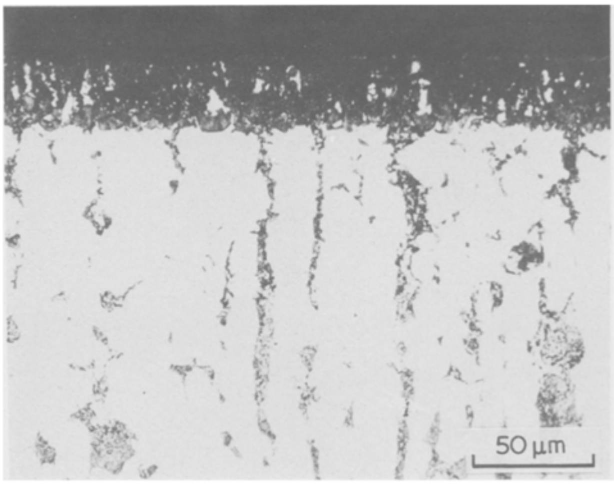

Figure 7 Plain carbon steel plasma nitrided in dissociated ammonia for 40 min at 923 K. Nital etch.

absence of any nitrogen source in the reactive gas stream by prenitriding the substrate. In addition, thicker titanium nitride coatings can be formed on prenitrided steel compared to plain steel under the same CVD conditions when nitrogen is included in the reactive atmosphere.

Little information is available on the iron–nitrogen system in the region of 1273 K, but the metastability of iron–nitrogen austenite and the iron nitrides is well-known [8]. Although the exact conditions prevailing at the surface of the steel during deposition are not clear, the nitrogen available from a pre-nitrided substrate will be located in the vicinity of the immediate surface. This is particularly true in the case of the ferritic nitrided substrate. The comparable thickness of the titanium nitride coatings on the austenitic nitrided and ferritic nitrided steels is interesting, but may not be significant. Austenitic nitriding of the steel offers the possibility of introducing a deeper high-nitrogen case which will either increase the amount of nitrogen available from the substrate or the amount of nitrogen, if any, which can be retained in the subsurface. However, austenitic nitriding also gives rise to porosity in the subsurface zone, which poses a practical limitation on its use as a pretreatment.

Porosity at the grain boundaries of nitrogen-containing austenite and other iron–nitrogen compounds such as epsilon iron nitride and carbonitride is well recorded (see, for example, [9–13]). Although some porosity may well be advantageous at the immediate surface of epsilon iron–carbonitride layers produced by ferritic nitrocarburizing [14], porosity formation during thermochemical treatments with nitrogen is generally considered undesirable.

It has been observed that homogeneous iron–nitrogen austenite can be prepared if thin sections [15] are nitrided at relatively low temperatures (863 to 1000 K) [11]. During carbonitriding [12] at constant time and temperature there is a threshold nitrogen activity necessary before porosity will occur and a reduction in porosity can be brought about by using low nitrogen activities, short treatment times and a low temperature. From this it would appear that porosity formation during the austenitic nitriding of a steel will be dependent upon treatment time, nitrogen activity and temperature, and that it may be possible

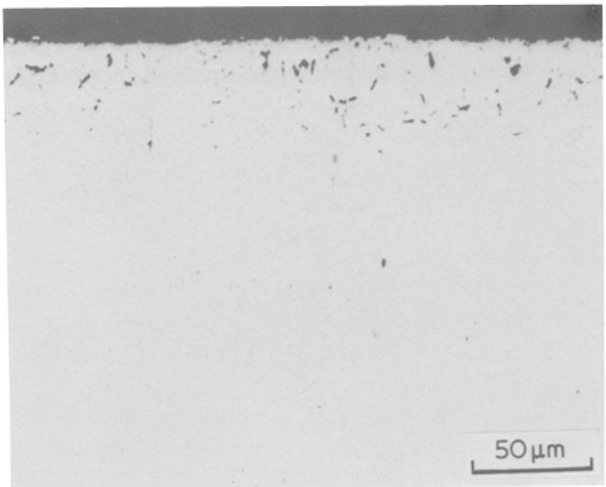

Figure 6 Plain carbon steel plasma nitrided in 5% N_2 to 95% H_2 for 6 h at 923 K. Etched with nital and repolished to illustrate porosity in subsurface region.

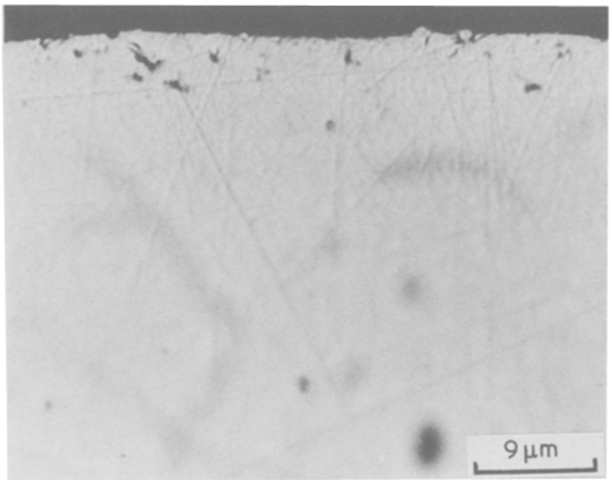

Figure 8 Plain carbon steel plasma nitrided in dissociated ammonia for 40 min at 923 K. Etched with nital and repolished to illustrate porosity in the subsurface region.

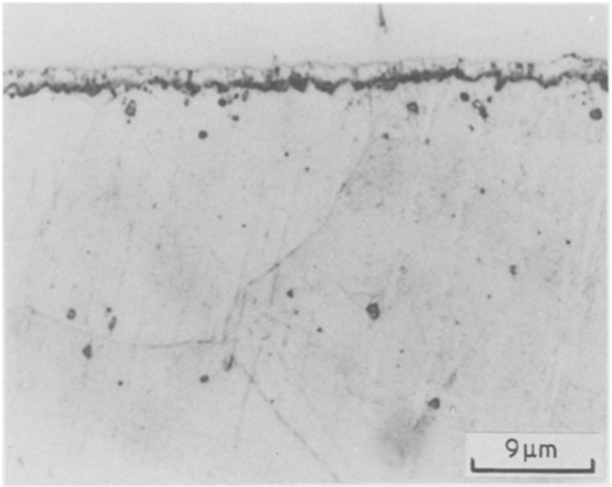

Figure 9 Plain carbon steel treated with a $TiCl_4-H_2-N_2$ gas mixture for 3 h at 1273 K. A thin layer of titanium nitride has formed at the surface. Nital etch.

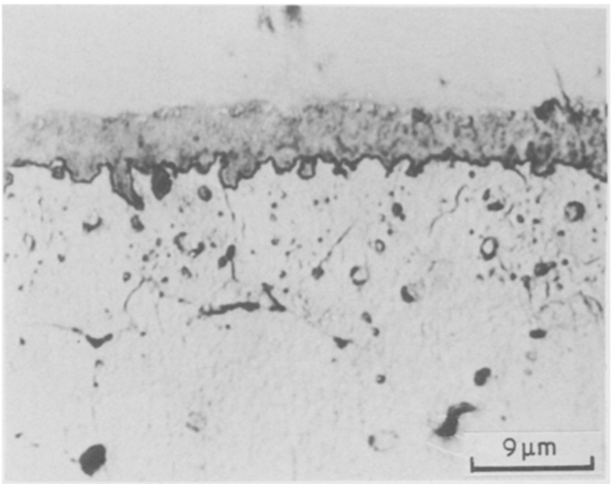

Figure 11 Austenitic nitrided plain carbon steel treated with a $TiCl_4-H_2-N_2$ gas mixture for 3h at 1273K. A layer of titanium nitride has formed at the surface. Porosity is present in the subsurface region. Nital etch.

to prepare a low-porosity nitrogen-containing austenite case on ferrous parts if appropriate control can be exercised over the nitriding process.

The austenitic nitriding temperature used in this work may be considered low from the point of view of producing iron–nitrogen austenite. One consequence of the low treatment temperature is that only a shallow case depth, approximately 50 μm, is developed after the maximum nitriding time employed. This case depth is shallow compared to those produced by commercial case-hardening methods such as a carburizing and carbonitriding [7]. It is significant from a practical standpoint that even by reducing the nitrogen content of the nitriding plasma to the minimum level at which the austenite phase is formed (5% N_2 was the limit observed here), and by operating at a low temperature, it has not been possible to eliminate porosity in an austenite case of approximately 50 μm thick on a plain carbon steel. The time dependence of porosity development is demonstrated by comparing the section of material austenitic nitrided for 6 h with that treated for only 40 min in a dissociated ammonia plasma (Figs 3 and 8). There is a reduction of porosity with a reduction of nitriding time over this interval with minimal porosity after 40 min. The case depth achieved is, of course, shallower after 40 min (compare Figs 2 and 7). In view of these findings on porosity it is concluded that the most appropriate prenitriding method for steel to be CVD coated with titanium nitride is a ferritic nitriding treatment.

5. Conclusions

1. The production of titanium nitride coatings by chemical vapour deposition from titanium tetrachloride–hydrogen–nitrogen gas mixtures at 1273 K on a plain low-carbon steel substrate is enhanced by nitriding of the substrate prior to deposition.

2. A titanium nitride coating can be produced by chemical vapour deposition on a steel surface using substrate-derived nitrogen only.

3. In practice, porosity may be reduced but not eliminated in the austenite case on plain low-carbon steel produced by austenitic nitriding using a nitrogen–hydrogen glow discharge plasma.

4. Ferritic nitriding is an appropriate method for introducing nitrogen to a steel substrate prior to chemical vapour deposition of titanium nitride to bring about the promotion of the formation of the coating.

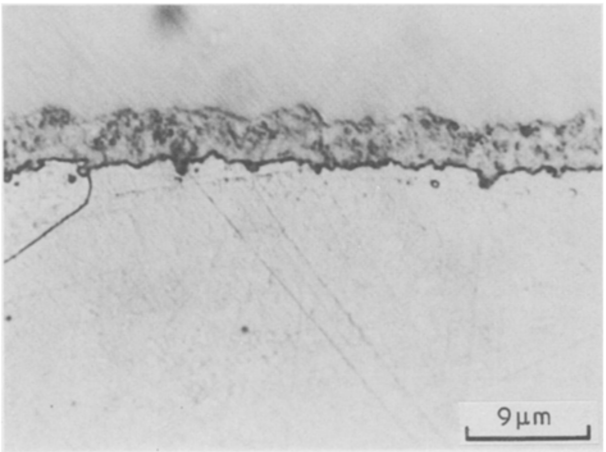

Figure 10 Ferritic nitrided plain carbon steel treated with a $TiCl_4-H_2-N_2$ gas mixture for 3 h at 1273 K. A layer of titanium nitride has formed at the surface. Nital etch.

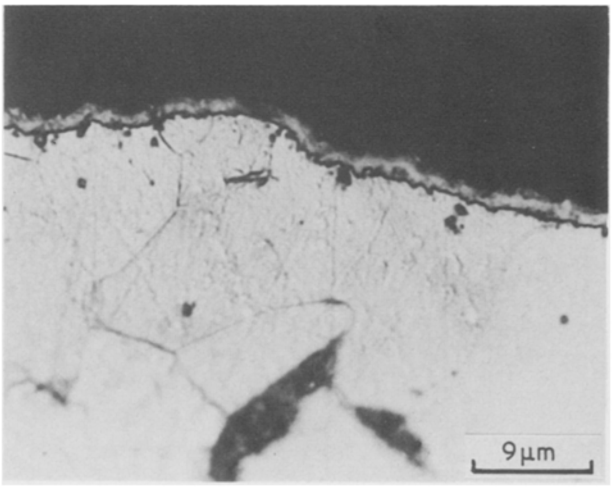

Figure 12 Ferritic nitrided plain carbon steel treated with a $TiCl_4-H_2$ gas mixture for 30 min at 1273 K. A layer of titanium nitride has formed at the surface. Nital etch.

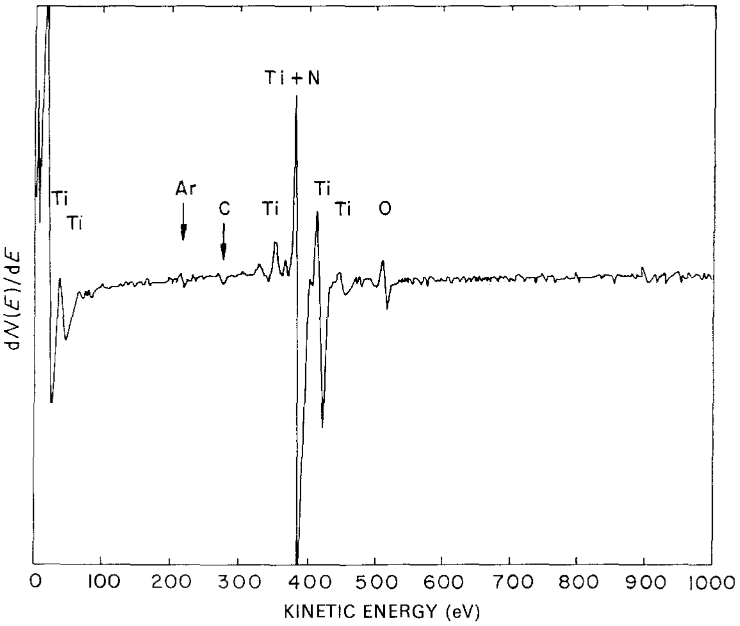

Figure 13 AES profile from the TiN layer on an austenitic nitrided steel, showing a minimal contribution of substrate-derived carbon to coating growth. Electron beam 3 keV, 50 nA. Pressure 3 × 10^{-8} Pa.

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