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TiC_xN_y and TiC_x-TiN films obtained by CVD in an ultrasonic field

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TiC_xN_y mono- and TiC_x–TiN double-layer films with a thickness of 30 to 100 μm were prepared on a carbon steel (C: 0.6 to 0.7%) substrate by CVD in an ultrasonic field (ultrasound frequency: 19 kHz; power: 10 to 20 W cm^{-2}). The moderate deposition conditions for obtaining an adherent and thick film of TiC_xN_y were: substrate temperature: 1050° C; H_2, N_2, $TiCl_4$ and CH_4 flow rates: 6.2, 4.0, 0.9 and 0.26 to 2.0 ml sec^{-1}, respectively. The growth rate, grain size and degree of ⟨2 2 0⟩ preferred orientation were found to decrease with increase in CH_4 concentration. TiC_xN_y film on carbon steel had a Vickers microhardness of 1800 to 2600 and an adhesion strength to the substrate of more than 120 kg cm^{-2}. A TiC_x–TiN ($x \sim 0.5$) double-layer film was obtained at 1050° C by a controlled alternative deposition of TiC_x or TiN. Quasi-epitaxial growth of crystallites in the double layers was found to prevail in both coatings of TiC_x(220)/TiN(220)/steel and TiN(200)/TiC_x(200)/steel.

1. Introduction

A thick film of TiN on an iron substrate was previously found to be deposited [1] using chemical vapour deposition (CVD) in an ultrasonic field. The adherence and toughness of a vapour-deposited film were found to be improved by radiation of an ultrasound to the substrate. In the present paper, the term "ultrasonic CVD" will be used for the CVD process by ultrasound radiation.

The CVD of TiC_xN_y and TiC–TiN films using ordinary processes has been studied by several workers. Titanium carbonitride was coated onto carbon fibres [2], steel [3–5] and other substrates [6] from the reactants of $TiCl_4 + CH_4$ (or CCl_4) + N_2 + H_2 [2, 3, 6] or $TiCl_4$ + $N(CH_3)_3$ (or $(CH_3)_2NH$) [4, 5]. A double-layer film of TiC–TiN was obtained by Schintlmeister *et al.* [7] and Nickl *et al.* [6]. In the present study, thick films of titanium carbonitride TiC_xN_y and a double-layer film of TiC_x–TiN were obtained on a carbon steel substrate by ultrasonic CVD. The purpose of this investigation is to prepare the adherent and tough, thick coating of TiC_xN_y mono- or TiC_x–TiN double-layer film on a carbon steel substrate. Deposition conditions, micro-structure and some properties of the deposits were investigated in detail.

The chemical reactions for producing TiC_x, TiN and TiC_xN_y are as follows:

$$TiCl_4 + xCH_4 + (2-2x)H_2 \rightarrow TiC_x + 4HCl \quad (1)$$

$$TiCl_4 + 1/2N_2 + 2H_2 \rightarrow TiN + 4HCl \quad (2)$$

$$2TiCl_4 + 2xCH_4 + yN_2 + 4(1-x)H_2 \rightarrow 2TiC_xN_y + 8HCl. \quad (3)$$

2. Experimental details

Fig. 1 shows a schematic diagram of the experimental apparatus, which is analogous to that used for the ultrasonic CVD of TiN [1]. An ultrasound with a source frequency of 19 kHz and a power of 10 to 20 W cm^{-2} is applied to the substrate. $TiCl_4$ vapour is carried with hydrogen gas to the reactor, keeping the temperature of the $TiCl_4$ evaporator at 70° C. H_2 and N_2 gases are purified in the activated copper and silica gel columns, while CH_4 gas is dehydrated by conc. H_2SO_4. The mixing ratio of CH_4 to N_2 in the reactant gas is kept constant during the run for the deposition of TiC_xN_y.

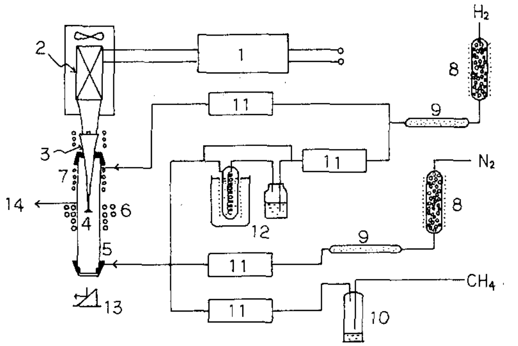


Figure 1 Schematic diagram of experimental apparatus. 1, oscillator; 2, vibrator; 3, horn; 4, carbon steel substrate; 5, quartz reactor tube; 6, r.f. induction coil; 7, cooling pipe; 8, activated copper; 9, silica gel; 10, conc. H_2SO_4; 11, flowmeter; 12, $TiCl_4$ saturator; 13, mirror; 14, outlet.

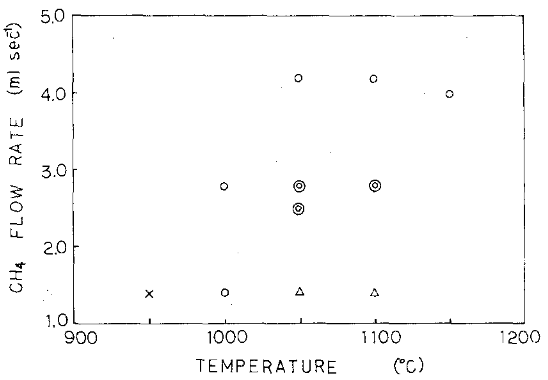


Figure 2 Dependence of substrate temperature and CH_4 flow rate. H_2, 6.2 ml sec^{-1}; $TiCl_4$, 0.9 ml sec^{-1}. x, no deposit; △, amorphous deposit; ○, TiC_x ($x \sim 0.4$); ◎; TiC_x ($x \sim 0.5$).

The TiC_x–TiN double-layer is deposited by controlling an alternative introduction of CH_4 or N_2 gas in the feed gas stream.

The substrate is a nailheaded carbon steel with a carbon content 0.6 to 0.7%, the tip of which is 7 mm diameter. After polishing the surface with emery paper (no. 1200), the substrate is silver-soldered to the horn, which is inserted into the reactor. The substrate is pre-cleaned with HCl aqueous solution and CH_3OH. Prior to a reaction run, the reaction chamber is flushed with H_2 gas for 30 min, and the substrate is pretreated at 1000° C for 2 min in a H_2 gas stream.

3. Results and discussion

3.1. Deposition conditions of TiN and TiC_x

A moderate deposition condition of TiN or TiC_x was established as the first step in obtaining a successful coating of TiC_xN_y or TiC_x–TiN by ultrasonic CVD. It was reported earlier [1] that a TiN coating on carbon steel (~ 0.3% C) could be obtained at a substrate temperature of 950 to 1100° C and gas flow rates of: H_2, 7.4 ml sec^{-1}; N_2, 2.0 to 5.0 ml sec^{-1}; and $TiCl_4$, 0.9 to 1.0 ml sec^{-1}. In the present study, the substrate temperature range was narrowed to 1000 to 1100° C. The gas flow rates were fixed as follows: H_2, 6.2 ml sec^{-1}; N_2, 4.0 ml sec^{-1}; and $TiCl_4$, 0.9 ml sec^{-1}.

In Fig. 2, the effects of substrate temperature and CH_4 flow rate on deposited species are shown to be especially correlated. A stoichiometric composition of $TiC_{1.0}$ cannot be formed in the temperature range used, but the composition of $TiC_{0.4}$ to $TiC_{0.5}$ is estimated by comparison of the measured lattice constant with those in the literature [8, 9]. The high thermal stability of CH_4 at relatively low temperatures below 1200° C results in the non-stoichiometry of the TiC_x product [10]. An amorphous deposit, presumably titanium carbide, is formed at CH_4 flow rates lower than 1.5 ml sec^{-1}. Therefore, the optimum deposition

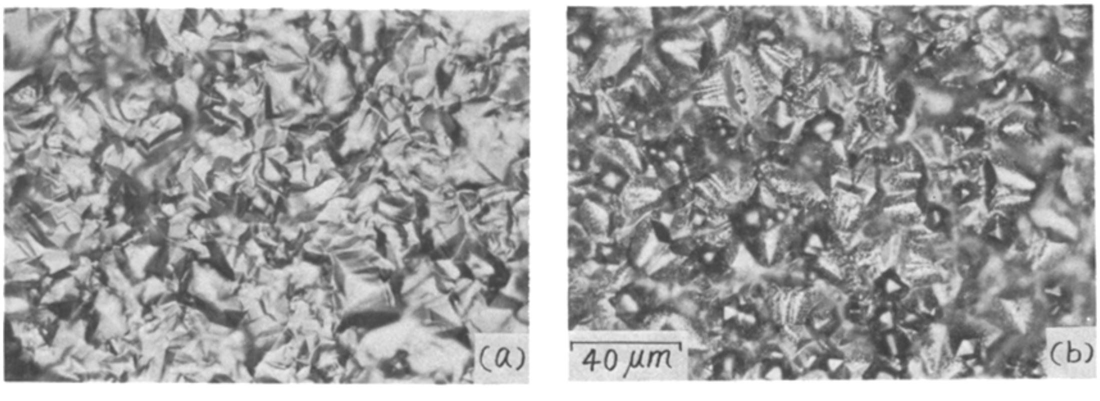


Figure 3 Surface appearance of vapour-deposited TiN and TiC_x. (a) TiN: 1000° C; H_2, 6.2 ml sec^{-1}; N_2, 4.0 ml sec^{-1}; $TiCl_4$, 0.9 ml sec^{-1}; (b) TiC_x: 1100° C; H_2, 6.2 ml sec^{-1}; CH_4, 2.5 ml sec^{-1}; $TiCl_4$, 0.9 ml sec^{-1}.

conditions of TiC_x ($x \sim 0.5$) were found to be: substrate temperature, 1050 to 1100° C; H_2, 6.2 ml sec^{-1}; CH_4, 2.5 ml sec^{-1}; $TiCl_4$, 0.9 ml sec^{-1}.

Fig. 3 shows the typical surface appearance of TiN or TiC_x ($x \sim 0.5$), which was obtained at the optimum deposition conditions described above. No cracking or peeling of the deposited film could be seen except at the rim part of the substrate. The TiN and TiC_x films obtained by ordinary CVD tend to be cracked or peeled off [1]. The nucleation of crystallites is considered to be accelerated by an ultrasonic agitation process of the gaseous diffusion layer in the vicinity of the substrate surface. The deposited surface of TiN or TiC_x was found by X-ray diffraction to have a strongly preferred orientation of ⟨2 2 0⟩ or ⟨2 0 0⟩, respectively, which is shown in Fig. 10.

3.2. Synthesis of TiC_xN_y coatings on carbon steel

Titanium carbonitride TiC_xN_y coatings were obtained under deposition conditions where the substrate temperature and the flow rates of H_2 and $TiCl_4$ were kept constant, only the CH_4 flow rate parameter being variable. A temperature of 1050° C was chosen as the substrate temperature and the reaction time was 30 min for every run. Fig. 4 shows the variation of X-ray diffraction patterns of TiC_xN_y as a function of CH_4 flow rate. Each pattern has a stronger line intensity of the (2 2 0) reflection, compared with ASTM patterns of TiN and TiC [11]. The degree of preference for the ⟨2 2 0⟩ direction is noted, however, to decrease with increasing CH_4 flow rate. The diffraction lines of TiC_xN_y are found to shift progressively to lower angles with increase in CH_4 flow rate.

The lattice constant measured by the lattice spacing of the (2 2 0) diffraction is plotted in Fig. 5 as a function of CH_4 flow rate (lower axis) or CH_4 concentration in the reactant gas (upper axis), where the lattice constant increases from the value of TiN ($a = 4.237$ Å), but the rate of this increase in lattice constant is apparently diminished at higher concentrations of CH_4. From a continuous increase of the lattice constant, a solid solution in the system TiC–TiN would be considered to be formed. Assuming the relationship between the lattice parameter and the composition of the TiC–TiN system given by Duwez *et al.* [12] and $x + y = 1$ in this case, the chemical compositions of TiC_xN_y were estimated to be $TiC_{0.3}N_{0.7}$ and $TiC_{0.4}N_{0.6}$, respectively, for the deposits which were obtained at CH_4 flow rates of 0.26 and 0.5 ml sec^{-1}.

The growth rate of TiC_xN_y film versus CH_4 flow rate is also illustrated in Fig. 5. A gradual decrease in the growth rate can be confirmed as the CH_4 flow rate increases. Fig. 6 shows scanning

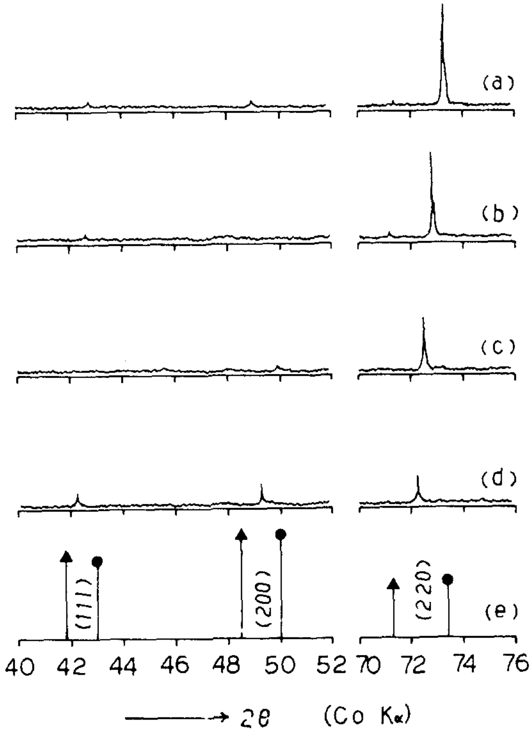


Figure 4 Variation of X-ray diffraction patterns of TiC_xN_y. Temperature, 1050° C; H_2, 6.2 ml sec^{-1}. N_2, 4.0 ml sec^{-1}; $TiCl_4$, 0.9 ml sec^{-1}. CH_4: (a) 0 ml sec^{-1}, (b) 0.5 ml sec^{-1}, (c) 1.0 ml sec^{-1}, (d) 2.0 ml sec^{-1}, (e) ASTM TiC (▲), TiN (●).

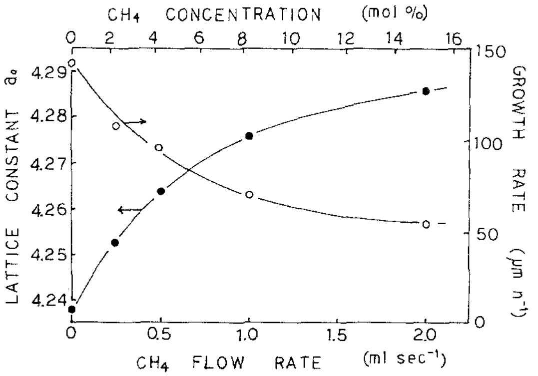


Figure 5 Lattice constant and growth rate of TiC_xN_y film. Temperature, 1050° C, H_2, 6.2 ml sec^{-1}. N_2, 4.0 ml sec^{-1}; $TiCl_4$, 0.9 ml sec^{-1}. ●——● Lattice constant, ○——○ growth rate.

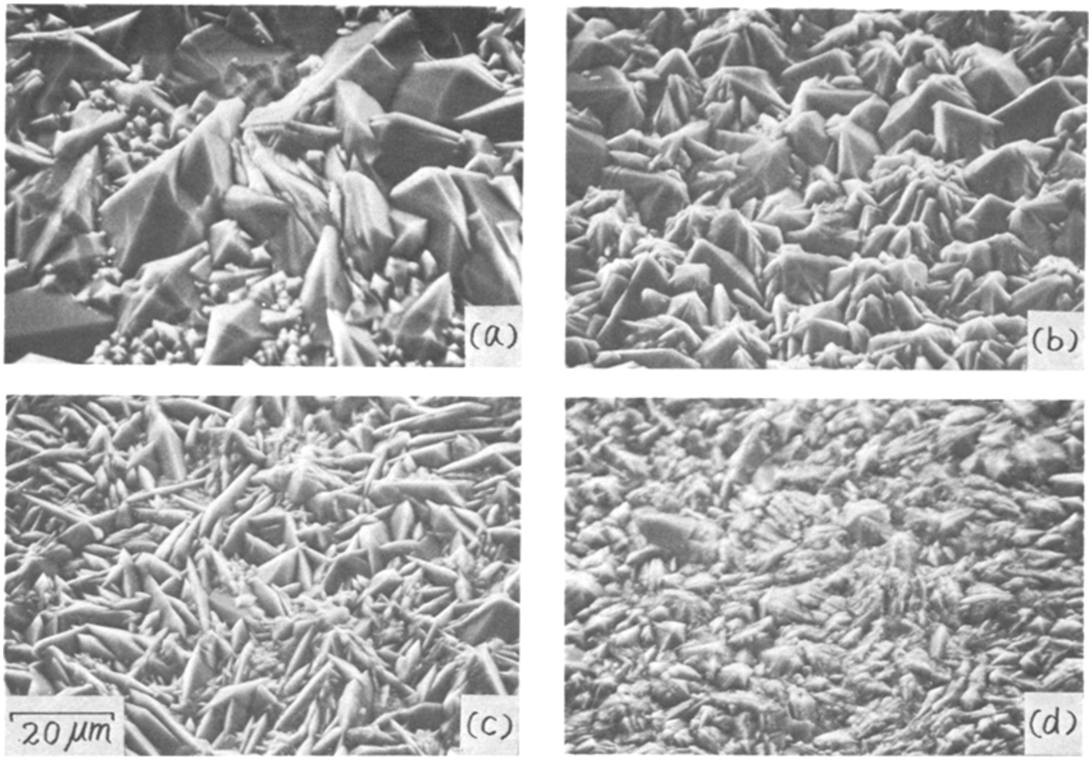


Figure 6 Scanning electron micrograph of the surface of vapour-deposited TiC_xN_y. Temperature, 1050° C; H_2, 6.2 ml sec^{-1}; N_2, 4.0 ml sec^{-1}; $TiCl_4$, 0.9 ml sec^{-1}. CH_4: (a) 0.26 ml sec^{-1}, (b) 0.5 ml sec^{-1}, (c) 1.0 ml sec^{-1}, (d) 2.0 ml sec^{-1}.

electron micrographs of TiC_xN_y, which were obtained at various CH_4 flow rates. The surface is composed of a number of grains where small crystallites adhere to the valleys between larger ones. The mean crystallite size decreases apparently from ~ 15 to 3 μm with the CH_4 flow rate. Rapid growth of a large crystallite would be depressed with an increase of carbon concentration in the feed gas, so that progressive decreases in the anisotropic growth (see Fig. 4) and the total growth rate (see Fig. 5) must result.

Fig. 7 shows micrographs of the cross-section of the TiC_xN_y coating. Uniform and adherent thick

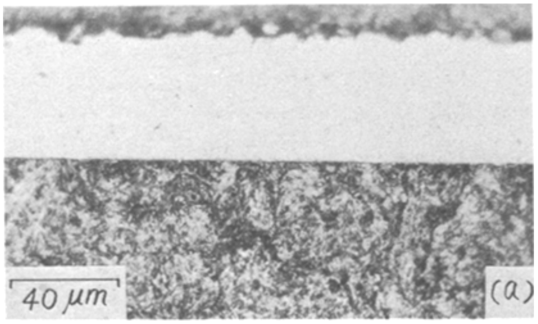
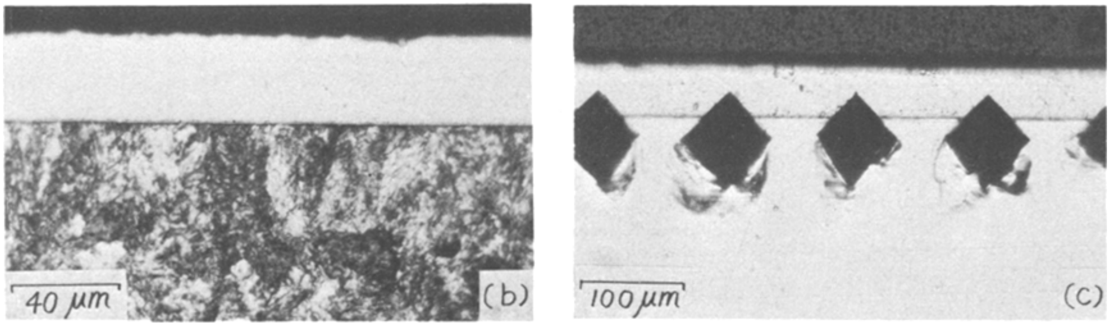


Figure 7 Micrograph of the cross-section of TiC_xN_y coating. Temperature, 1050° C; H_2, 2.6 ml sec^{-1}; N_2, 4.0 ml sec^{-1}; $TiCl_4$, 0.9 ml sec^{-1}. CH_4: (a) 0.5 ml sec^{-1}, (b) 2.0 ml sec^{-1}, (c) 0.26 ml sec^{-1}.



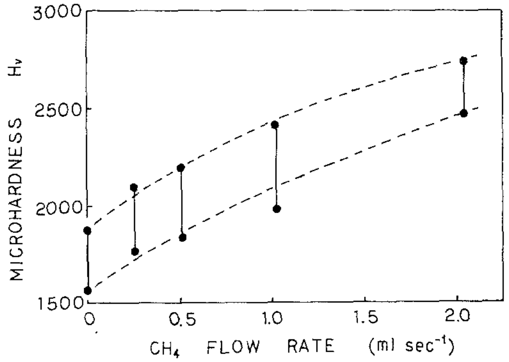


Figure 8 Vickers microhardness versus CH_4 flow rate. Substrate temperature, 1050° C; H_2, 6.2 ml sec^{-1}, N_2, 4.0 ml sec^{-1}; $TiCl_4$, 0.9 ml sec^{-1}.

films ((a) and (b)) can be seen on the carbon steel substrates which were etched by nital solution (C_2H_5OH:HNO_3 = 100:5). In order to appreciate the adherence of the film (see Fig. 7c), the interface region between the TiC_xN_y film and carbon steel substrate was indented under 1 kg load using a microhardness test machine. No peeling occurs even with loads of 10 indentations at intervals of about 40 μm. The specimen surface was then adhered to the test jig with an inorganic adhesive (adhesion stength: 120 kg cm^{-2}), and the fracture strength was measured using a tensile testing machine. Fracture occurred at the interface between the TiC_xN_y film and the test jig, which verifies the adhesion strength of the film to exceed 120 kg cm^{-2}.

Fig. 8 shows the plots of Vickers microhardness of the cross-section of TiC_xN_y (100 g load) versus CH_4 flow rate. The microhardness of a specimen varies relatively from place to place with a tendency to increase as the CH_4 flow rate increases. The measured hardness values (1800 to 2600) are found to be between those of TiN and TiC reported in the literature [1,9].

3.3. Quasi-epitaxial growth of TiN–TiC_x double-layer coating

A TiN–TiC_x double layer was deposited on carbon steel using reactions 1 and 2 so as to evaluate the possibility of obtaining a multilayer film of $(TiN–TiC_x)_n$ by an "intermittent CVD". Fig. 9 shows the cross-section of the coating TiC_x/TiN/Steel (i.e. TiC_x layer on TiN layer on carbon steel substrate) or the coating TiN/TiC_x/Steel (TiN layer on TiC_x layer on carbon steel substrate). The optimum deposition parameters of the substrate temperature and flow rate of H_2 or $TiCl_4$ were kept constant during the processes shown in Table I, at 1050° C, 6.2 and 0.9 ml sec^{-1}. The other parameters (reaction time and gas flow rates) in the first and the subsequent processes

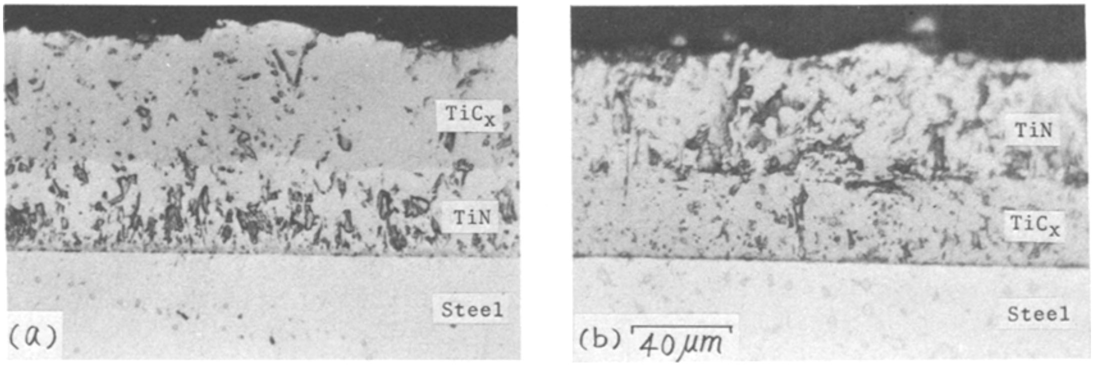


Figure 9 Micrograph of the cross-section of TiC_x/TiN or TiN/TiC_x double layer on carbon steel.

TABLE I Deposition conditions of TiC_x–TiN double-layer films

Deposited film	Deposition parameter	1st process	2nd process
(a) TiC_x/TiN/steel	N_2 flow rate (ml sec^{-1})	4.0	0
	CH_4 flow rate (ml sec^{-1})	0	2.5
	Reaction time (min)	15	40
(b) TiN/TiC_x/steel	N_2 flow rate (ml sec^{-1})	0	4.0
	CH_4 flow rate (ml sec^{-1})	2.5	0
	Reaction time (min)	30	15

Temperature; 1050° C; H_2, 6.2 ml sec^{-1}; $TiCl_4$, 0.9 ml sec^{-1}.

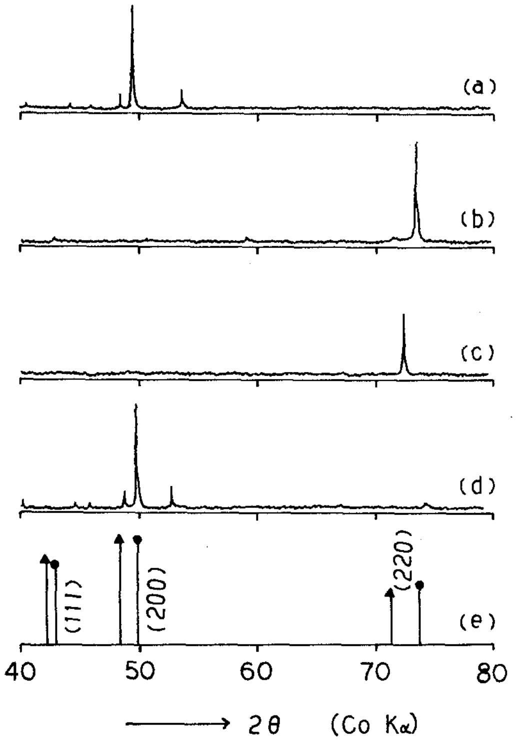


Figure 10 X-ray diffraction patterns of mono- and double layer surfaces. (a) TiC_x/steel, (b) TiN/steel, (c) TiC_x/TiN/steel, (d) TiN/TiC_x/steel, (e) ASTM TiC (▲) and TiN (●).

were chosen, as shown in Table I. Thick double-layer films of TiC_x/TiN and TiN/TiC_x are apparent in the figure. The adherence between the TiC_x layer and the TiN layer was found to be very good, even when the double-layer film was peeling from the substrate.

Fig. 10 shows the X-ray diffraction patterns of the specimen surface of mono- and double-layers of TiC_x and TiN. As described in Section 3.1, TiC_x and TiN have their inherent strongly preferred orientations to the directions ⟨2 0 0⟩ and ⟨2 2 0⟩, respectively (see Fig. 10a and b), although some unknown diffraction lines with weak intensities appear in the pattern of TiC_x. Fig. 10c and d are patterns of the surface of the films, TiC_x/TiN/Steel and TiN/TiC_x/Steel, respectively, which show ⟨2 2 0⟩ and ⟨2 0 0⟩ preferred orientations. It is suggested from these patterns that a quasi-epitaxial growth of crystallites prevails in the growth of TiC_x (2 2 0) on TiN (2 2 0), or TiN (2 0 0) on TiC_x (2 0 0).

Schintlmeister *et al.* [7] obtained a fine crystalline, smooth coating of TiN on TiC, while Nickl *et al.* [6] found the epitaxy of TiN on the (1 0 0) TiC single crystal. Our results would support quasi-epitaxial growth. It is of interest in our data in Fig. 10 that the epitaxial growth of the second layer occurs independent of its inherent preferred orinetation. Fig. 11 shows a micrograph of the boundary region between the TiC_x/TiN layers which are oriented to the ⟨2 2 0⟩ direction. A continuous columnar structure of epitaxially grown crystallites is found to penetrate both textures of TiC_x and TiN.

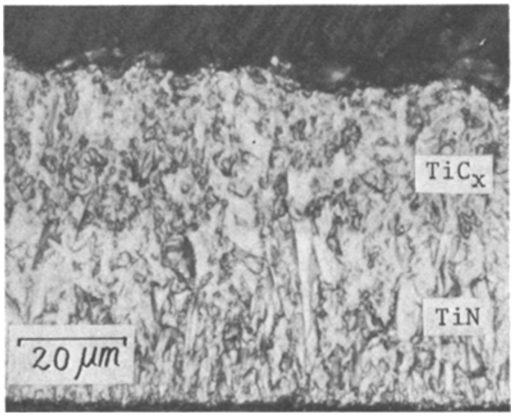


Figure 11 Micrograph of the boundary region between the TiC_x and TiN layers.

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