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Effect of chromium in substrate steel on the chemical vapour deposition of TiC

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TiC coatings on tools are widely used in order to increase their wear resistance. Chemical vapour deposition of TiC was performed on steels having different chromium contents in order to find a relationship between the chromium content in steel and the deposition characteristics of TiC. In the initial growth stage, the nucleation and growth was found to be strongly affected by the chromium content of the substrate steel. This result was attributed to the diffusion of carbon through the chromium-rich phase. Chromium element which increases the activation energy of carbon diffusion through the substrate steel reduces the deposition rate. A strongly preferred orientation of the (2 2 0) axis in the growth direction was found. Scanning electron micrographs showed that the grain was equiaxed for all experimental deposition conditions. They also showed that the grain size became finer with increasing chromium content in the substrate steels. Wear-resistance was improved with decreasing TiC grain size.

1. Introduction

The high-performance tooling employed for many mechanical working processes requires a combination of wear resistance and mechanical toughness. This combination can be achieved satisfactorily by coating the surface of a tough steel substrate with a hard wear-resistant material such as a titanium carbide deposited by the chemical vapour deposition (CVD) method [1]. Ruppert and co-workers studied titanium carbide coatings on carbon or iron containing chromium above 800° C [2–5]. Semenova and Minkevich investigated titanium carbide coatings on 12% substrate steel on the deposition TiC has not been clearly established. In the experiments, deposition was performed only through the substrate reaction, which is the reaction between adsorbed $TiCl_4$ and carbon which is diffused from the substrate steel. The present work was concerned with the effects of the chromium content of the substrate steel on the growth rate, surface morphology, and the preferred orientation of TiC deposited on to different kinds of substrate steel. The apparent activation energy for carbon diffusion in the substrate steel was evaluated and the wear resistance of deposited TiC was also examined.

2. Experimental procedure

The titanium carbide coating is obtained by means of reactions between titanium tetrachloride and carbon which is diffused from the substrate steel at temperatures of 900 to 1050° C. Chemically the reaction can be described in the following way

$$TiCl_4 + C\ (\text{in substrate}) + 2H_2 \rightarrow TiC + 4HCl$$

A schematic diagram of the experimental apparatus is shown in Fig. 1. $TiCl_4$ vapour was bubbled into the deposition reactor using hydrogen as the carrier gas and the temperature of the $TiCl_4$ bubbler was kept at 50° C throughout all the experiments. The flow rate of $TiCl_4$

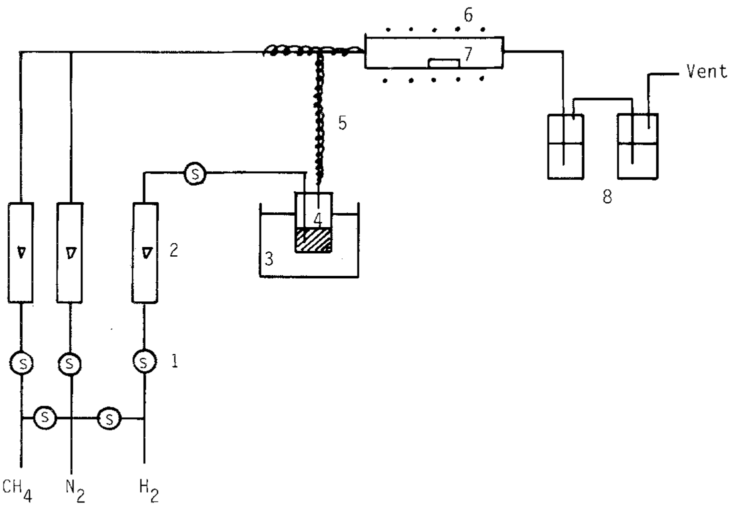

Figure 1 Schematic diagram of the CVD apparatus: 1, solenoid value; 2, flowmeters; 3, water bath; 4, $TiCl_4$ evaporator; 5, heating coil; 6, resistance furnace; 7, substrate; 8, alkali traps.

TABLE I Deposition conditions for a TiC coating

Temperature (° C)	Time (min)	Total pressure (torr)	Flow rate ($cm^3 min^{-1}$)			Chromium content in 1.0 wt % C–Cr substrate (wt %)
			$TiCl_4$	CH_4	H_2	
900 950 1000 1050	10, 30, 60, 80, 100	400	60	0	2940	0, 5, 11, 13
900 950 1000 1050	30, 60, 80, 100	400	37.5	0	2962.5	0
900 950 1000 1050	30, 60, 80, 100	400	75	0	2925	5

was controlled by changing that of the hydrogen carrier gas. The deposition reactor was an alumina tube, with an inner diameter of 44 mm and a length of 1000 mm. The temperature of the specimen was controlled by the k-type thermocouple contacted to the substrate. In the experiments, the total pressure of reactor was kept at 400 torr. The experimental conditions for TiC deposition are listed in Table I. The substrate steels used in the experiment were 1.0 wt % carbon steel and the chromium steels containing 5, 11, and 13 wt % Cr, with the dimensions of 4 × 10 × 5 mm^3. The preferred orientation of the deposited TiC layer was investigated using an X-ray diffractometer with $CuK\alpha$ radiation and a nickel filter. The texture coefficient of deposited TiC was calculated by using the measured integrated intensities from the equation;

$$\mathrm{T.C.}\,(h\,k\,l) = \frac{I(h\,k\,l)}{I_0(h\,k\,l)}\left[\frac{1}{n}\sum_{1}^{n}\frac{I(h\,k\,l)}{I_0(h\,k\,l)}\right]^{-1}$$

where $I(h\,k\,l)$ is a measured intensity of the $(h\,k\,l)$ plane, $I_0(h\,k\,l)$ is the standard intensity of the ASTM standard powder pattern diffraction data, and n is the number of reflections [7]. Scanning electron microscopy (SEM) was used to examine the surface morphologies of the TiC deposits. The coating thickness was determined by two methods; first, the weight increase after coating and second, the observation of the cross section through an optical microscope. The wear-resistance of the deposited TiC was investigated by a pin-on-disc method as shown in Fig. 2. The tip of the pin which was used in the wear test was pasted with diamond powder. The rotation speed of the specimen was kept at 480 r.p.m. and a load of 1 kg was applied to the pin.

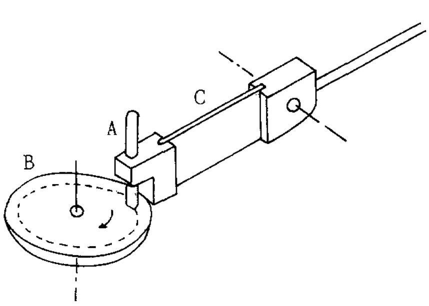

Figure 2 Wear test machine, A, pin specimen: B, disc specimen; C, spring plate.

3. Results and discussion

3.1. Effect of deposition time on the growth rate of TiC

The dependence of the increase in weight of TiC on deposition time for various kinds of substrate steels at the deposition temperature of 1000° C is illustrated in Fig. 3. Takahashi *et al.* [8] reported coating experiments on 0.8 wt % carbon steel without supplying hydrocarbon from the gas phase leading to a considerable TiC thickness. They found a linear relationship between the thickness of the TiC layer and the square root of time which suggests that the rate-controlling process is the carbon diffusion in the TiC layer or in the substrate, respectively. From the results, we believe that TiC deposition by the substrate reaction is controlled by the carbon activity in the substrate steel. In case of TiC deposition onto high chromium steels, a very long incubation time was observed and the deposition rate decreased with increasing chromium content. Because the straight lines do not go through the origin, Lindstrom and Amberg [9] attribute this deviation to the superimposed hydrocarbon reaction for high alloyed steels in the case of a gaseous reaction. However, in the study, deposition experiments were conducted only using the substrate reaction without supplying hydrocarbon from the gas phase. The chromium content in the substrate steel decreases the carbon activity and retards the diffusion rate of the carbon [10]. Therefore, we believe that the chromium in the substrate steel retards the nucleation and initial growth of TiC.

The morphologies of TiC deposited at 1000° C for 1 h are shown in Fig. 4. The grain size of the deposited TiC decreases with increasing of chromium content in the substrate steels. In particular, the grain size of TiC deposited on a low chromium steel is much larger than that on a high chromium steel as shown in Fig. 4. We concluded that the chromium content of the substrate steel had a considerable influence on the growth morphologies of a deposited TiC layer. Table II shows the

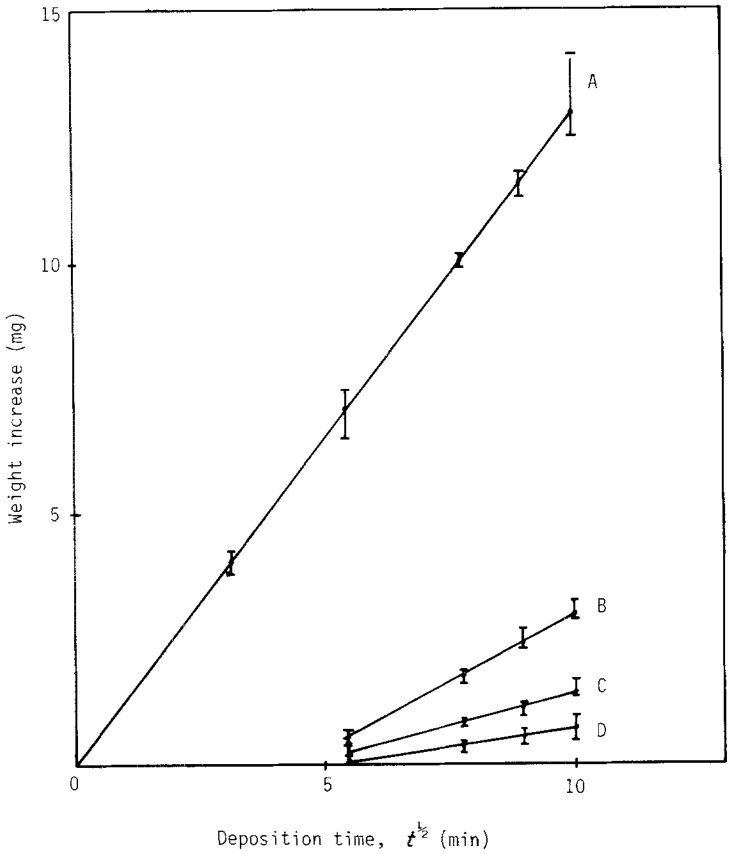

Figure 3 Increase in weight of the coating layer with deposition time for different substrates. Deposition temperature, 1000° C; P_{TiCl_4}, 0.020 atm. (A) 1.0 wt % C; (B) 1.0 C–5 wt % Cr; (C) 1.0 wt % C–11 wt % Cr; (D) 1.0 wt % C–13 wt % Cr.

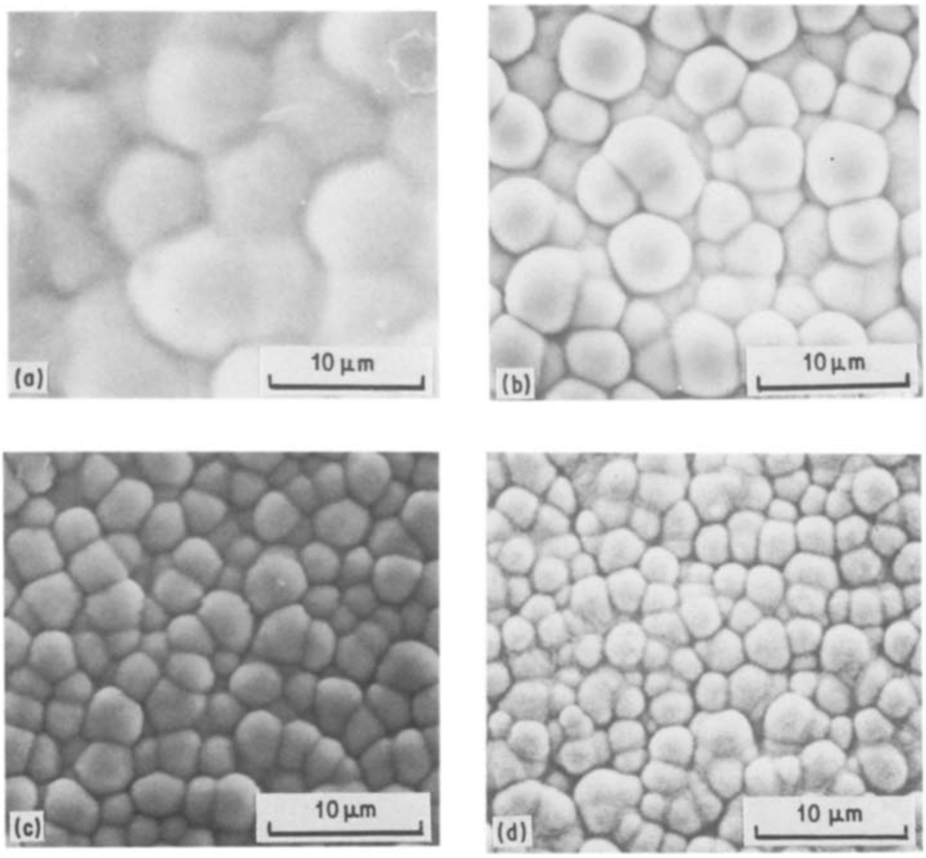

Figure 4 Scanning electron micrographs of the surface appearance of the TiC coating for different substrates. Deposition temperature, 1000° C; deposition time, 1 h; P_{TiCl_4}, 0.020 atm. (a) 1.0 wt % C; (b) 1.0 wt % C–5 wt % Cr; (c) 1.0 wt % C–11 wt % Cr; (d) 1.0 wt % C–13 wt % Cr.

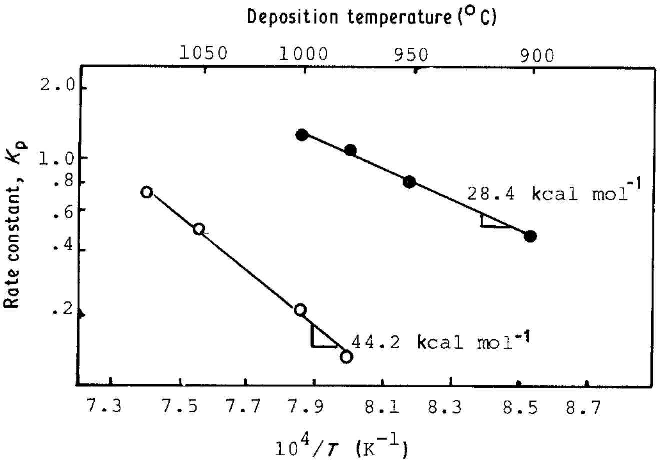

Figure 5 Dependence of reaction rate constant on the reciprocal temperature for different substrates. (●) Substrate, 1.0 wt % C; P_{TiCl_4}, 0.013 atm. (○) Substrate, 1.0 wt % C–5 wt % Cr; P_{TiCl_4}, 0.026 atm.

variation of X-ray diffraction intensities and texture coefficients of each crystallographic plane of TiC crystals deposited at 1050° C over 90 min. Texture coefficients of the (2 2 0) plane of TiC have large values in specimens deposited onto substrate steel containing a small amount of chromium, but have a slightly small value with increasing of chromium content. However, it can be seen that the TiC crystals grow with (2 2 0) preferred orientation from the results of Fig. 4 and Table II.

3.2. Calculation of apparent activation energy for carbon diffusion in the substrate steel

The TiC layer grows by accumulation of the reaction product by quasi-steady state diffusion. The relation of TiC weight increase to deposition time is $\Delta W = K_p t^{1/2}$ where ΔW is the weight increase of the TiC layer, K_p is the reaction rate constant independent of deposition time, and t is the deposition time. As the carbon diffusion in the substrate steel is a thermally activated process, the dependence of the reaction rate constant on deposition temperature is $K_p = A_s \times \exp(-Q_d/RT)$ where A_s is the frequency constant, Q_d is the apparent activation energy for carbon diffusion and T is the absolute temperature. An Arrhenius plot of the reaction rate constant against deposition temperature is shown in Fig. 5. A least mean square analysis of the slopes in Fig. 5 shows that the apparent activation energies are 28.4 and 44.2 kcal mol^{-1} for TiC deposited on substrate steel without chromium and with 5 wt % chromium content, respectively. This result shows that the activation energy for carbon diffusion increases with increasing tendency to form carbides.

3.3. Wear characteristics of TiC-coated substrate steels

Film failure for the thicker films was found to occur in two stages [11]. (1) Early in the wear cycle, small semi-circular brittle cracks formed in the wear track. (2) The density of these brittle cracks increased during the wear cycles until the cracks linked up in certain regions of the wear track and strips of films were removed. The rates of wear as a function of deposition temperature of TiC deposited for 100 min are shown in Fig. 6. The wear rate of TiC deposited on 5 wt % chromium steel varied little over the experimental temperature range, while that on the substrate steel without chromium content increased with increasing deposition temperature. Fig. 7 shows the relationship of cumulative weight loss of TiC deposited on different kinds of substrate steel to the test time. The

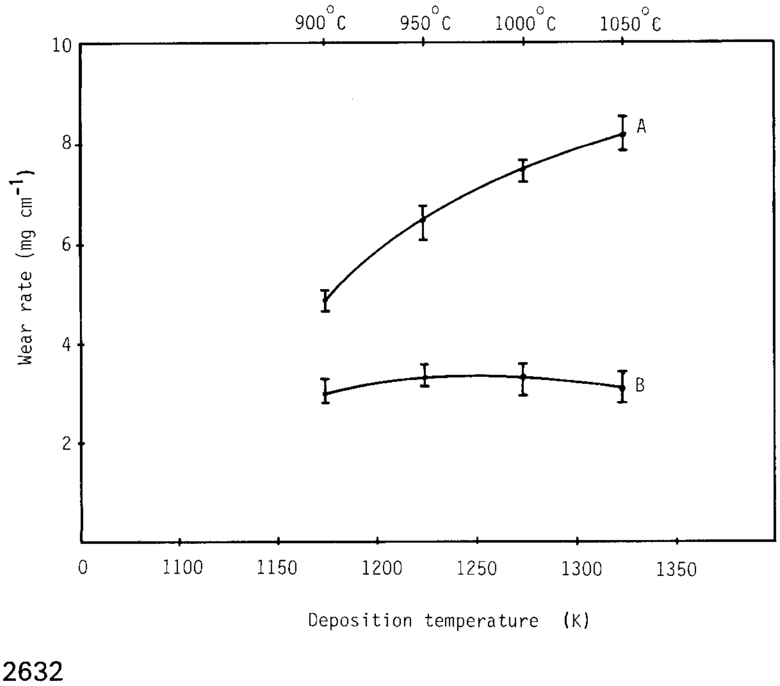

Figure 6 Rate of wear as a function of different deposition temperatures of TiC deposited for 100 min. (A) 1.0 wt % carbon steel. (B) 5 wt % chromium steel. Load on the pin, 1 kg; rotation speed of the specimen, 480 r.p.m.; test time, 40 min.

TABLE II X-ray diffraction intensities and texture coefficients of TiC crystals

$(h k l)$	I_0	I and T.C. for the following substrates							
		1.0 wt % C		1.0 wt % C–5 wt % Cr		1.0 wt % C–11 wt % Cr		1.0 wt % C–13 wt % Cr	
		I	T.C.	I	T.C.	I	T.C.	I	T.C.
111	80	68	0.9	49	0.7	85	0.9	88	0.9
200	100	76	0.8	57	0.7	100	0.8	100	0.8
220	50	100	2.1	100	2.3	81	1.4	89	1.4
113	30	13	0.5	13	0.5	24	0.7	27	0.7
222	10	8	0.8	7	0.8	15	1.3	15	1.2

Deposition temperature, 1050° C; deposition time, 90 min; P_{TiCl_4}, 0.020 atm.

weight loss of the specimen deposited on 5 wt % chromium steel increased slightly with increasing test time, while that on the substrate steel without chromium abruptly increases. As shown in Figs 6 and 7, the chromium content in the substrate steel has a considerable influence on the wear resistance of deposited TiC. Chromium in the substrate steel decreases the carbon activity in the substrate steel and retards the diffusion of carbon which forms the TiC. Therefore, chromium in the substrate steel decreases the growth rate of the TiC layer and decreases the grain size of TiC crystals. This result is shown in Fig. 8. The wear resistance of TiC deposited on 5 wt % chromium steel is superior to that on the substrate steel without chromium content.

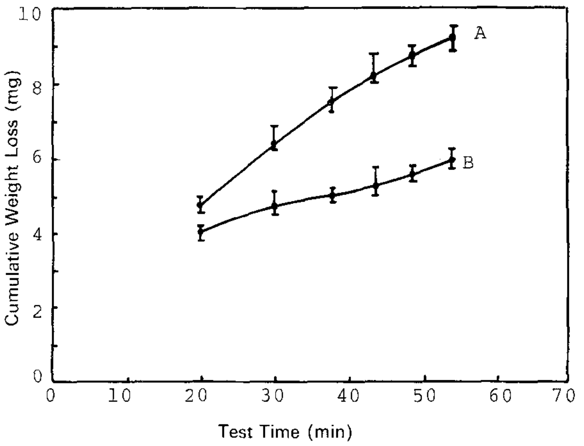

Figure 7 The relationship of cumulative weight loss of TiC deposited on different kinds of substrate steel to the test time. (A) 1.0 wt % carbon steel, P_{TiCl_4}, 0.013 atm; (B) 5 wt % chromium steel, P_{TiCl_4}, 0.026 atm.

4. Conclusion

We have shown a considerable influence of the chromium in the substrate steel on the growth rate. The deposition rate and the texture coefficient of the (2 2 0) plane of deposited TiC decrease with increasing chromium contents in the substrate steel. The apparent activation energy of carbon diffusion in the steel substrate having 5 wt % chromium is about 44.2 kcal mol^{-1}, while that of a steel substrate without chromium is 28.4 kcal mol^{-1}. Therefore, chromium increases the activation energy for carbon diffusion in the substrate steel. As the chromium content in the substrate steel retards the nucleation and initial growth of TiC, the effect of incubation time was studied. The grain size of the deposited TiC decreases with increasing chromium content in the substrate steels and the wear-resistance of TiC was also improved.

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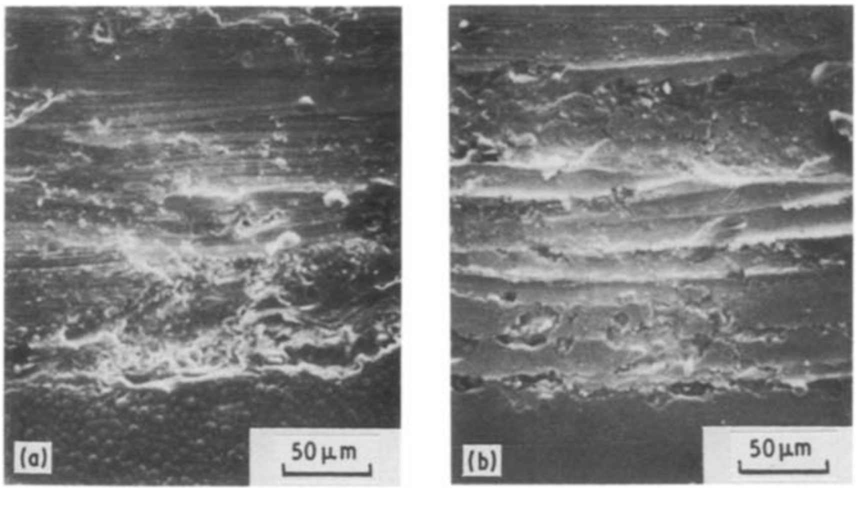

Figure 8 Scanning electron micrographs of the wear of TiC coating deposited by substrate reaction at 1000° C for 1 h (a) 1.0 wt % carbon steel; (b) 5 wt % chromium steel.

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