EFFECT OF OPERATING TEMPERATURE ON STRUCTURE PROPERTIES OF TiC_x NANOPARTICLE COATING APPLIED BY PACVD

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Titanium carbide (TiC) is a widely used hard coating to improve the wear resistance and lifetime of tools because of its outstanding properties such as high melting point, high hardness, corrosion resistance and abrasion resistance. These properties were drastically improved by using nanotechnology. So in this project, TiC_x was applied on hot-working die steel (H11) by Plasma CVD (PACVD). The effect of operating temperatures on TiC_x structure properties have been studies by

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typical and advanced analyses methods such as SEM, XRD, FTIR and Raman. The best properties of TiC_x nanoparticle, such as nanostructure, mechanical properties and chemical properties, were obtained at 480 °C.

Keywords: Titanium carbide (TiC_x); Plasma CVD; Nanostructure; Coating

1. Introduction

Recently, transition-metal carbides, such as TiC , are becoming very attractive in the field of decorative films due to their interesting combined mechanical and physical properties.^{1,2}

These coating are characterized by high hardness and a high melting point,³ excellent electrical and thermal conductivity, high chemical and thermal stability, and good wear and corrosion resistance.⁴⁻¹⁰ Due to this unique combination of properties, these materials have been extensively investigated and systematically used in many technological applications to improve significantly tool life.⁴⁻¹⁰

It has been shown that some applications greatly benefited from a nanostructured phase for TiC_x . Indeed production of nanostructured TiC_x thin films has been recently carried out by several methods. The frequent technique to deposit TiC is chemical vapour deposition; however, because of the high temperature during deposition, even tool steels need an additional heat treatment after coating. In contrast, physical vapour deposition allows lower substrate temperature in the range of 200- 500 °C to be applied, and thus an additional heat treatment can be avoided.¹¹ Another method is plasma-assisted chemical vapour deposition (PACVD), which has the main advantage that coating of uniform thickness and composition can be produced even on substrates with a complex shape. the most important factor on applied TiC_x nanostructure coating by PACVD is kinetic parameters, such as temperature, methane partial pressure, time, and plasma voltage. Among these parameters, temperature was playing important role on the final composition and properties of TiC_x nanostructure coating.¹¹⁻¹³

In this paper TiC_x nanoparticle coating was applied by PACVD on hot-working die steel (H_{11}), and then the effect of operating temperature on structure properties of TiC_x have been studies by typical and advanced analyses methods such as SEM, XRD, FTIR and Raman.

2. Experimental

2.1. TiC_x nanoparticle coating deposition

TiC_x nanostructure coating was deposited in a PACVD reactor using a TiCl_4 - CH_4 - H_2 - Ar gas mixture. The plasma was created using an A.c. pulse power supply. The PACVD TiC_x deposition was conducted in the same industrial-set plant, as shown schematically in Fig. 1. The cylindrical vacuum chamber, which is 350 mm in diameter and 400 mm in height, can be heated with an auxiliary heating system, the temperature of which is controlled by a thermocouple. Substrates were placed on cylindrical cathodes and kept at a negative potential. The surrounding wall of the chamber is used as the anode. The hot –

working die steel (AISI H₁₁) were used as substrate materials. The pressure in the reaction chamber amounted to 8 mbar. For more details concerning the deposition conditions see Table 1. AISI H₁₁ substrate in the form of $\Phi 10 \times 5$ mm was quenched and tempered to a hardness of 300 HV. Cylinder samples after polishing to about R_a 2 μ m using an Al₂O₃ slurry, the samples were first cleaned with acetone and then ultrasonically cleaned in ethanol and a short sputtering process in an Ar and H₂ plasma prior to deposition. The substrate temperature was achieved by the ion bombardment an auxiliary heating system was changed by an auxiliary heating system. Three kinds of operating temperatures (such as 470, 480 and 490 °C) were selected for investigating the Influence of operating temperature on structure properties of TiC_x nanoparticle coating.

2.2. Measurements

The surface morphology, uniformity, homogeneity, and its cracks for coated samples were examined by XL-30 (PHILIPS) scanning electron microscopy (SEM) and the phase of the coating was determined by X-ray diffraction (XRD) (by using a Philips PW-1730 diffractometer in continuous scanning mode and using Cu K α radiation ($\lambda = 0.154056$ nm)). The infrared (IR) reflectance of the coatings and (by using Fourier Transform Infrared Spectrometer (FTIR)) and Raman spectroscopy (by using Raman spectra were recorded with Raman spectrometer).

Fig. 1. Schematic diagram of PACVD system

Table 1. Process parameters for the deposition of TiC_x

parameter	
Pulsed voltage (V)	590
Pressure (mbar)	3-10
Duty cycle (%)	33
Process time (h)	4
H ₂ (NL/min)	1.6
Ar(NL/min)	0.05
TiCl ₄ (carrier H ₂). (NL/min)	0.05
CH ₄ (NL/min)	0.4- 3.2

3. Result and Discussion

3.1. Detecting of TiC_x nanoparticle coating

Applied TiC_x nanoparticle coating on metals is so difficult, because this compound is metastable, and reaction between atoms in PACVD method is complicated. Among several parameters which have an important effect on properties of TiC_x coating, operating temperature has an essential role as a thermodynamic and kinetic parameter.

In order to understand the mechanism of structure evolution with variation of operating temperature, XRD analysis was carried out. Fig. 2 shows the XRD diffraction patterns for the deposited samples with different operating temperature, such as 470, 480 and 490 °C. The reference peaks of TiC_x , obtained from JCPDS value. In this figure, increasing operating temperatures cause to intensity of detected peak were increased, but, this would be consistent with the fact that no signs of a TiC-type phase were detected by XRD, These peaks move to higher angles (comparing with the stress free TiC lattice) with increasing operating temperature from 470 to 490 °C, due to various compound between Ti- C and residual stress in the TiC_x structure.¹⁴⁻¹⁷

Fig.2. XRD patterns of the TiC_x nanoparticle coatings deposited by PACVD, with different operating temperatures.

In order to detecting the TiC_x composition of the samples and, in particular identify the chemical bonding of the species that were not directly evident from the XRD results, SEM, EDX, FTIR and Raman measurements were performed on the samples.

Fig. 3 shows SEM picture of TiC_x nanoparticle coating in three kinds of temperatures, such as 470, 480 and 490 °C, in this figure the best homogeneity and uniformity access at 480 °C, following, The TiC_x nanoparticle coating was deposited at 480 °C is selected for another analyses such as, the FTIR, Raman and EDX measurement.

Fig. 3. SEM micrographs of TiC_x nanoparticle coating deposited at (a) 470°C, (b) 480°C, (c) 490°C.

Fig. 4 shows FTIR spectra of the film, in this figure the Ti-C^{18} bands at lower wave numbers was shown. However, the broad bands about 390 and 420 cm^{-1} corresponds generally to vibration mode from TiC_x since it was this phase that was found to be dominant on the XRD results.

Fig. 4, shows Raman spectroscopy of films, This result is similar to that reported by Zehnder and Patscheider, who could identify non-carbidic carbon upto $44\text{ at.}\%$ of Ti .¹⁹

Fig. 4. Infrared reflectivity spectra of the TiC_x nanoparticle coating deposited at $480\text{ }^{\circ}\text{C}$.

Fig.5. Raman spectra of TiC_x nanoparticle coating deposited at $480\text{ }^{\circ}\text{C}$.

The presence of Ti-O-Ti characteristic modes on this film corresponds to TiO_2 compounds, the limited bands about 480 , 1563.7 , 1455 and 1684.1 cm^{-1} corresponds generally to vibration mode from Ti-O-Ti , C-C , C-O and C=O ¹⁴, respectively, and also the limited bands about 1318.8 and 1359.4 cm^{-1} corresponds commonly to vibration mode from DLC.¹⁷ Two strong peaks positioned at approximately 266.8 and 586.6 cm^{-1} and identified as Ti-C were visible. All these Raman shifts are in good agreement with formerly published results.²⁰

Fig. 6 shows EDX measurement of the films indicated the sharp peak of Ti and a little percent Cl (resulting from TiCl_4 as a precursor). So, these results obtained from XRD, EDX, FTIR and Raman analyses signified that the phase of coating is TiC_x nanoparticle.

3.2. Effect of operating temperature on the phase composition

Operating temperature is one of the most important parameters in applied TiC_x nanoparticle coating by PACVD method. In this paper, the effect of three kinds of operating temperatures, such as 470, 480 and 490 °C, were investigated on the phase composition of TiC_x nanoparticle coating.

Fig. 6. EDX measurement of TiC_x nanoparticle coating deposited at 480 °C.

Fig.2 indicates that the TiC (111) peak for the TiC_x coating show s a small (almost negligible) shift to higher angles compared to the JCPDS value, and confirmed that the number of peaks and their intensity was raising with increasing operating temperature from 470 to 490 °C. This is in agreement with the theoretical results of Hugosson et al.²¹ However, there is a substantial shift of the TiC (111) peak to higher angles, because increasing operating temperature lead to enhanced reaction between carbon atoms and titanium atoms and resulting applied a homogeneous and uniform TiC_x nanoparticle coating on hot-working die steel (H_{11}).

Fig. 5 shows SEM picture of TiC_x nanoparticle coating in three kinds of temperatures, such as 470, 480 and 490 °C, in this figure the best homogeneity and uniformity access at 480 °C.

To determine the crystallite size of the coatings, the grain size was determined from the full width half maximum (FWHM) of the X-ray peaks using the Scherrer equation “Eq. (1)”:²²

$$\text{Grain size} = 0.9\lambda/\cos\theta \text{ FWHM} \quad (1)$$

where λ is the wavelength of the incident radiation and θ the Bragg angle. On the assumption that peak broadening is due to grain size variation only, the grain size for TiC_x for three kinds of temperatures, such as 470, 480 and 490 °C was summarized in table 2.

Table 2. grain size of TiC_x nanoparticle coating at different temperature

Temperature (°C)	Grain size (nm)
470	80-130
480	20-40
490	90-120

The grain size of TiC_x nanoparticle coating was increasing with raising operating temperature from 470 to 480 °C, probably, it is related to formation of a uniform and stable plasma atmosphere on substrate at 480 °C rather than 470 °C, and also increasing operating temperature by means of accelerating reaction between carbon and titanium atoms, cause to applied homogeneous and uniform TiC_x nanoparticle coating on hot-working die steel (H_{11}). Indeed, stable plasma decreased activation energy of formation Ti-C , and lead to enhance number of TiC_x nucleation and finally the grain size of TiC_x nanoparticle was reduced. In this paper, was shown that stability of plasma atmosphere on substrate was decreased by Increasing operating temperature from 480 to 490 °C, so, the activation energy for formation TiC_x nanoparticle is raising and the number of TiC_x nucleation is decreased, finally the grain size of nanoparticle was gradually increased at 490 °C rather than 480 °C.

4. Conclusion

The formation of a stable plasma atmosphere in the PACVD method, results in homogeneous and uniform TiC_x nanoparticle coating. Operating temperature has an important effect on the stability of plasma atmosphere; however, uniform plasma creates at 480 °C, so, the number of TiC_x nucleation increases, the activation energy decreases and leads to applying a uniform TiC_x nanoparticle coating on hot-working die steel (H_{11}). The grain size of TiC_x nanoparticle coating which applied at 480 °C is about 20 to 40 nm.

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