VSiC Coating with High Oxidation Resistance and Excellent Tribological Property

Satoru Habuka1, Katsushige Shimizu[1] and Koji Abe[1]

[1]DOWA Thermotech Co., Ltd, Aichi 467-0854, Japan

Vanadium carbide (VC) coating has been widely used as wear-resistant hard coating on forging dies for its high hardness and good tribological property. In recent years, oxidation resistance is also required for hard coatings in addition to hardness and tribological property, as the processing conditions become more severe such as hot stamping, stamping of high tensile strength steel and processing with poor lubrication. Therefore, applying VC coating for such high-load processing is difficult due to its low oxidation resistance. For improving its oxidation resistance, Vanadium silicon carbide (VSiC) coating was developed by adding silicon (Si), an element that imparts oxidation resistance to the VC coating.

The VSiC coatings was deposited on HSS substrate using the PECVD (Plasma Enhanced Chemical Vapor Deposition) method. The composition, structure and hardness were investigated by using EPMA (Electron Probe Micro-Analyzer), XRD (X-ray Diffraction), Raman spectroscopy and nanoindentation. The oxidation resistance was evaluated by examining the changes in chemical composition and hardness after heating in an atmospheric environment. No significant change in composition and hardness was observed even after being heated to 800℃. This result shows VSiC coating has high oxidation resistance compared with that of VC coating.

Tribological properties of the VSiC coating were evaluated using the ball-on-disk test method with S45C ball. The results showed that VSiC coatings with lower carbon content had higher friction coefficients (≒0.8) and a larger amount of adhesions within the sliding tracks. On the other hand, as the carbon content increased, the friction coefficient decreased (<0.2), and simultaneously, the amount of adhesions within the sliding tracks decreased. The results of Raman spectroscopy for samples with higher carbon content showed the presence of amorphous carbon in the coating. Consequently, it is suggested that amorphous carbon in VSiC coating contributes to suppressing formation of adhesions and attaining excellent tribological property.

Keywords: *vanadium silicon carbide, plasma-enhanced chemical vapor deposition, oxidation resistance, amorphous carbon, low friction coefficient, adhesion resistance*

1. Introduction

Over the past few decades, coatings of transition metal nitrides and transition metal carbides have been utilized to improve the lifespan of cutting tools and dies due to their high wear resistance.[1, 2)] In recent years, severe machining conditions for cutting tools and dies, for example hot stamping, stamping of high-tensile steel and processing in poor lubricative condition, raise the surface temperature of coatings, leading to issues with oxidation wear of coatings. Consequently, high-oxidation-resistant coatings containing elements like Al [3-5)] , Cr [4)], and Si [5)] have been developed and are widely used today.

Vanadium carbide, known for its high hardness and excellent sliding characteristics [6,7)] , has been commonly employed in dies for press processing and cold forging. However, the lack of oxidation-resistant elements lowers its oxidation initiation temperature and prevents its use in high-load environments.

This study aims to achieve coating with both high oxidation resistance and exceptional tribological property by adding oxidation-resistant element to vanadium carbide.

2. Experiment

Vanadium silicon carbide (VSiC) coatings were deposited on high-speed tool steel substrate by pulsed direct current plasma-enhanced chemical vapor deposition (PECVD) using a gaseous mixture of VCl_4, SiH_3CH_3, CH_4, H_2 and Ar. Figure 1 shows a schematic view of the PECVD system used in this study. The substrate was placed on the charging plate (cathode of the system). The wall of chamber was the anode of the system and grounded. The pulsed voltage during deposition was controlled between 1000 V and 1400 V to keep the current of glow discharge constant and the frequency was 25 kHz. The pressure of chamber was kept at 60 Pa during deposition.

The specimens of this study were made of high-speed tool steel (SKH51 regulated in Japanese Industrial Standards). The specimens were mechanically polished to a mirror finish and cleaned using acetone before placed on the charging plate.

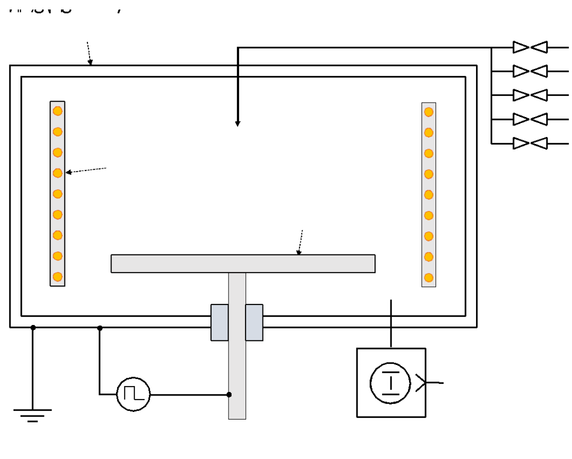

Figure 1 Schematic view of the PECVD system.

The chemical composition of the coatings was determined using electron probe micro analysis (EPMA, JEOL JXA-8530F). The structure of the coatings was evaluated using X-ray diffraction (XRD, Rigaku SmartLab CoK_{α}) at glancing incidence (θ=1°) and Raman spectroscopy (JASCO NRS-5100) with a laser wavelength of 532.0 nm.

Oxidation resistance of the coating was evaluated by comparing chemical composition and hardness before and after heating in the air at 800℃ for 1 hour.

1

Tribological property of the coatings was evaluated using the ball-on-disk test method under a load of 5 or 10 N at a sliding speed of 16.7 cm·s^{-1}. The tests were conducted using 6 mm diameter carbon steel (S45C regulated in Japanese Industrial Standards) balls as the counterpart at 25℃ and at 40% humidity in air without applying lubricants.

3. Results and discussions

3.1 Composition and hardness

Figure 2 shows the chemical compositions of VSiC coatings deposited with different CH_4 flow rate. The carbon content in the VSiC coating increases from 29.9 to 66.7at.% as the flow rate of CH_4 increases from 0 ml·min^{-1} to 10 ml·min^{-1}.

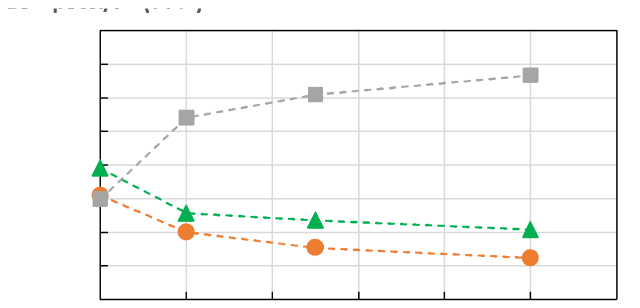

Figure 2 The chemical compositions of VSiC coatings as a function of the CH_4 flow rate.

Figure 3 shows indentation hardness of VSiC coatings with different carbon contents. The indentation hardness increased up to 50at.% of carbon content, and then decreased.

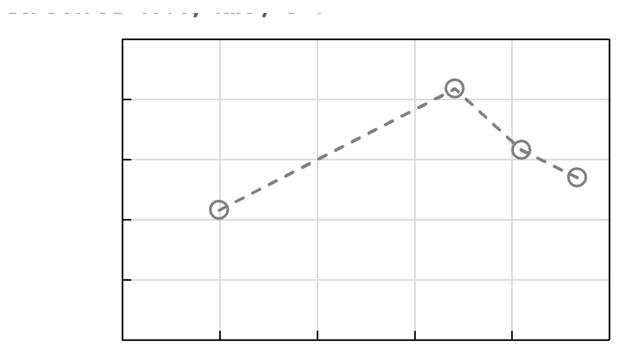

Figure 3 Effect of carbon content on indentation hardness of the VSiC coating.

3.2 Structure

Figure 4 shows XRD pattern of VSiC coatings with different carbon contents. These XRD patterns show that vanadium and silicon combine to form V_3Si in the VSiC coating with a carbon content of 50at.% or less, whereas all vanadium and silicon exist as carbides in the coating with more than 50at.% carbon content. Furthermore, absence of Si and SiC peak indicates that Si in the VSiC coating exist in an amorphous state. Additionally, considering that vanadium and silicon form V_3Si instead of VSi_2, it is inferred that SiC is preferentially formed compared to VC.

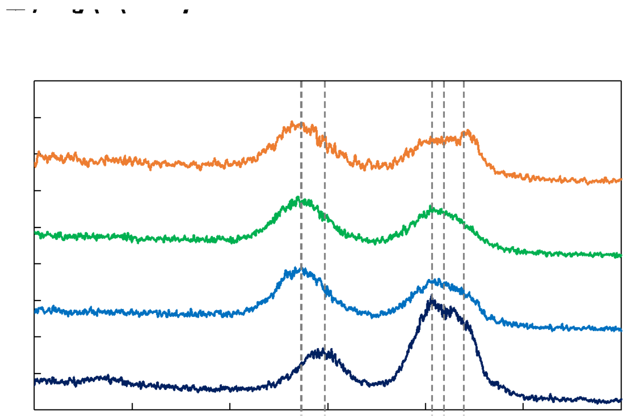

Figure 4 The XRD pattern of VSiC coatings with different carbon content.

Figure 5 shows the Raman spectra of VSiC coatings with different carbon contents. As the carbon content of VSiC coatings increases, growth of amorphous carbon peak was observed. These Raman spectra show that carbon first combines with vanadium and silicon to form carbides, and after all the vanadium and silicon have become carbides, carbon atoms then bond together to become amorphous carbon.

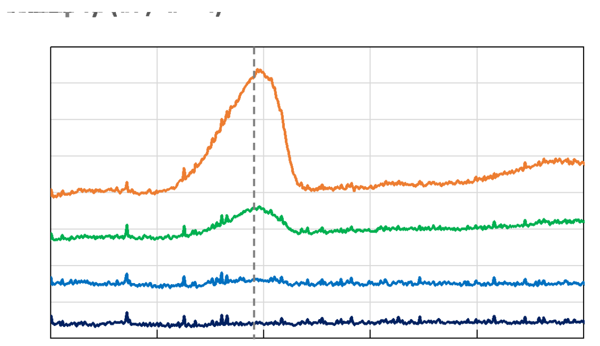

Figure 5 The Raman spectra of VSiC coatings with different carbon content.

These results suggest that the increasing of hardness shown in Figure 3 is related to the change of crystal structure revealed by the XRD measurements. Additionally, it is also suggested that the decreasing of hardness shown in Figure 3 is related to the increasing of amorphous carbon.

3.3 Oxidation resistance

To evaluate oxidation resistance of VSiC coating, we compared chemical composition and hardness before and after heating in the air at 800℃ for 1 hour. Table 1 shows changes in composition and hardness induced by the oxidation test. The result of the same test using VC coated specimen is also shown in table 1 as reference. After being heated to 800℃, no significant changes in composition and hardness were observed on the VSiC coated specimen. Whereas only few vanadium and carbon were observed in the case of the VC coated specimen. This result shows the VSiC coating has high oxidation resistance compared with that of VC coating.

Table 1 Comparison of composition and hardness before and after oxidation test.

	VSiC		VC	
	before	after	before	after
V (at.%)	15	17	50	2.7
Si (at.%)	24	26	-	-
C (at.%)	61	58	47	9.4
Fe (at.%)	-	-	-	73
hardness (GPa)	25.8	22.8	27.6	not measurable

3.4 Tribological property

Figure 6 shows the results of ball on disk test using VSiC coatings with different carbon contents. VSiC coatings with high carbon contents exhibited very low friction coefficients (<0.2). On the other hand, VSiC coatings with low carbon contents exhibited much higher friction coefficients (0.6-0.9).

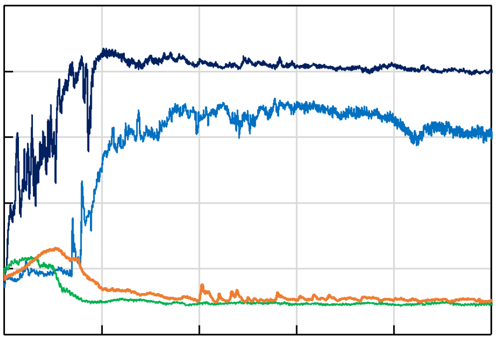

Figure 6 Comparison of friction coefficients of VSiC coatings with different carbon content.

Figure 7 shows the wear marks on VSiC coatings after the test. In the wear marks on specimens with low carbon content (high friction coefficient), numerous adhesions were observed. On the other hand, in the wear marks on specimens with high carbon content (low friction coefficient), such adhesions were not observed. These results indicate that amorphous carbon contained in VSiC coating with high carbon content not only reduce the friction coefficient but also prevents the deterioration of sliding characteristics caused by the generation of adhesions.

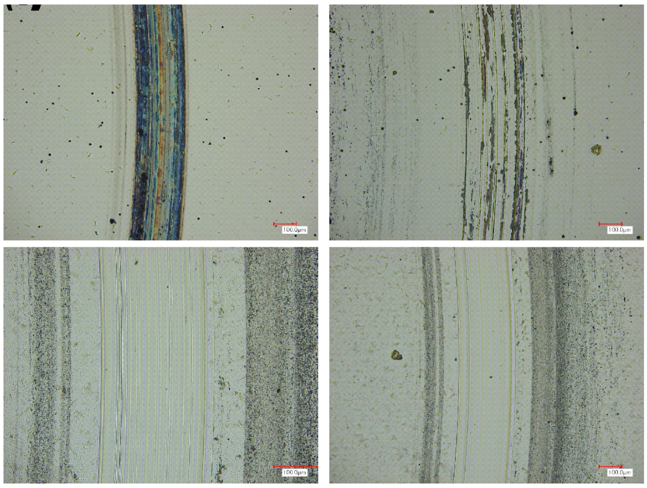

Figure 7 Wear marks on VSiC coatings after the ball on disk test.
(a) V 0.31-Si 0.39-C 0.30, (b) V 0.20-Si 0.26-C 0.54, (c) V 0.15-Si 0.24-C 0.61, (d) V 0.12-Si 0.21-C 0.67

4. Conclusion

The VSiC coatings with various carbon content have been deposited on high-speed tool steel substrate using PECVD method by changing the flow rate of CH_4 gas. The summary of our results is as follows:

1) Carbon content of VSiC coating affects its structure and the difference of structure is reflected on its hardness.
2) Heating at 800℃ in the air has no significant effect on the chemical composition and hardness of VSiC coating. Consequently, VSiC coating has high oxidation resistance compared with that of VC coating.
3) Amorphous carbon contributes to excellent tribological property of VSiC coating by not only reducing the friction coefficient but also preventing the generation of adhesions.

References

1) J.-E. Sundgren, H.T.G. Hentzell: Journal of Vacuum Science & Technology A **4** (1986) 2259-2279.
2) C. Mitterer, F. Holler, D. Reitberger, E. Badisch, M. Stoiber, C. Lugmair, R. Nöbauer, Th. Müller, R. Kullmer: Surface & Coatings Technology **163–164** (2003) 716–722.
3) P. Zhu, F. Ge, S. Li, Q. Xue, F. Huang: Surface & Coatings Technology **232** (2013) 311–318
4) R. Franz, C. Mitterer: Surface & Coatings

Technology **228** (2013) 1–13
5) I.-W. Park and K.H. Kim: Journal of Materials Processing Technology **130–131** (2002) 254–259.
6) B. Chicco, W.E. Borbidge, E. Summerville: Materials Science and Engineering: A **266** (1999) 62–72
7) P. Stoyanov, J. Schneider, M. Rinke, S. Ulrich, E. Nold, M. Dienwiebel, M. Stüber: Surface & Coatings Technology **321** (2017) 366–377.