

Influence of remaining C on hardness and emissivity of SiC/SiO₂ nanocomposite coating

J. Yi ^{a,*}, X.D. He ^a, Y. Sun ^a, Y. Li ^a, M.W. Li ^b

^a Center for Composite Materials, Harbin Institute of Technology, P.O. Box 3010, Harbin 150001, PR China

^b School of Materials Science and Engineering, Harbin Institute of Technology, P.O. Box 428, Harbin 150001, China

Received 10 February 2007; accepted 17 February 2007

Available online 22 February 2007

Abstract

SiC/SiO₂ nanocomposite coating was deposited by electron beam-physical vapor deposition (EB-PVD) through depositing SiC target on pre-oxidized 316 stainless steel (SS) substrate. High melting point component C remained and covered on the surface of ingot after evaporation. When SiC ingot was reused, remaining C had an effect on the composition, hardness and emissivity of SiC/SiO₂ nanocomposite coating. The composition of ingot and coating was studied by X-ray photoelectron spectroscopy (XPS). The influence of remaining C on hardness and spectral normal emissivity of SiC/SiO₂ nanocomposite coating was investigated by nanoindentation and Fourier transform infrared spectrum (FTIR), respectively. The results show that remaining C has a large effect on hardness and a minor effect on spectral normal emissivity of SiC/SiO₂ nanocomposite coating.

© 2007 Elsevier B.V. All rights reserved.

Keywords: Vapor deposition; Composition fluctuations; Optical spectroscopy

1. Introduction

SiC is a promising multi-function protective coating material for metal thermal protection systems (MTPS) because of their combination of unique physicochemical and mechanical properties in rigid condition, such as ultra high velocity and temperature condition [1–4]. Besides the excellent resistance to elevated temperature, oxidation, corrosion and ray radiation, SiC also possess the properties of high hardness, low friction coefficient and high emissivity. Furthermore, because of low thermal conductivity and high oxidation resistance, SiO₂ can act as an additive oxidation insulator layer between SiC nanocomposite coating and MTPS to increase oxidation resistance of MTPS [5–7]. When reusable space vehicle flies with hypervelocity, surface temperature of the section using SiC/SiO₂ composite coating mainly comes from the friction between air and vehicle surface. One hand, SiC/SiO₂ composite coating of low friction factor reduces surface friction heat. On the other hand, high emissivity of SiC/SiO₂ composite coating

can make it radiating a quantity of thermal energy to atmosphere, and reduce surface temperature of space vehicle and inward heat transfer.

EB-physical vapor deposition (PVD) method is usually used for fabricating nanocomposite films and coatings. The principle of this operation is to heat a ingot to evaporation point by electron beam (EB) in a vacuum chamber [8,9]. However, when vapor balance time is not sufficient during evaporation, high melting point component will remain and cover on the surface of ingot after evaporation, which has an effect on the composition, hardness and emissivity of coating in next evaporation for reused ingot. During EB-PVD preparing SiC/SiO₂ composite coating, high melting point component C remains and covers on the surface of reuse SiC ingot, and has an effect on the composition, hardness and emissivity of coating. In this paper, it is researched that the influence of remaining C covering on the surface of ingot on the composition, hardness and emissivity of SiC/SiO₂ nanocomposite coating.

2. Experimental

SiC/SiO₂ nanocomposite coatings were deposited on pre-oxidized 316 SS substrate by EB-PVD. SiC ingot of 98.5 mm in

* Corresponding author. Tel.: +86 451 8640 2345; fax: +86 451 8640 2477.
E-mail address: yj_hit@163.com (J. Yi).

diameter and 150 mm in length is placed into a water-cooled copper crucible of 100 mm in diameter. Due to a large volume, SiC ingot is repetitively used many times. Ahead every evaporation, SS substrate and molten pool both had been hold 10 min at evaporation temperature. The substrate temperature was kept around 1000 °C, the distance between ingot and substrate was 150 mm and the pressure of vacuum chamber was maintained at about 9.0×10^{-3} Pa during deposition. In this paper, preparing one SiC/SiO₂ nanocomposite coating sample is defined as evaporation one time. The surface area of all substrates was almost same, and all data were transformed to the same experimental condition.

The surface chemistry analysis of ingot and nanocomposite coating was carried out by XPS (PHI 5700, USA) using AlK α radiation at 1486.6 eV. The hardness of coating was characterized using a Nano Indenter XP instrument (MTS, Oak Ridge) with a diamond Berkovich indenter at a load of 2 mN. And nanohardness of every sample was tested for six times at different point and the nanohardness value of every sample was an average result. The spectral normal emissivity of nanocomposite coating was investigated by FTIR (IFS66, Bruker).

3. Results and discussion

3.1. Surface composition analysis of SiC ingot

After evaporation, one layer of black mater covered on the surface of molten pool zone in ingot. XPS analysis shows that there is only C element and no Si element existing in this layer. The peak at 284.8 eV represents graphite, which identified that SiC occurred decomposition and formed graphite during EB heat (shown in Fig. 1). As to each evaporation, it is quite difficult to evaporate the analytical C remaining in SiC ingot at the earlier stage of evaporation, since the saturated vapor pressure of C is much less than that of Si and SiC. At the same time, C is lighter than Si and SiC. As a result, remaining C will float on the outer surface of ingot in the progress of evaporation, and cover the surface of molten zone after evaporation. With the increase of evaporation times, the amount of C remaining at the

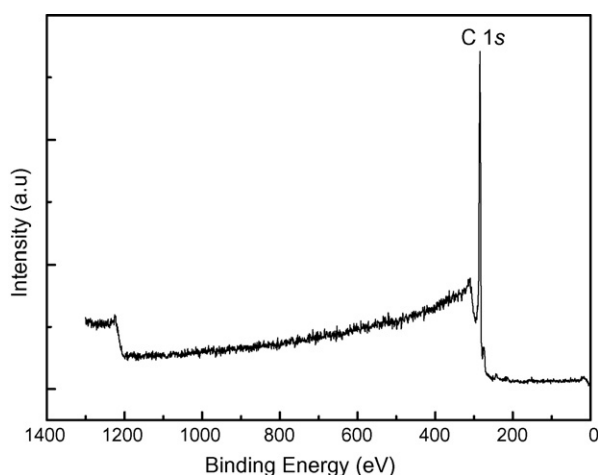


Fig. 1. XPS spectrum of the outer surface of molten pool zone in SiC ingot.

surface of ingot is also improved, which affect the time reaching evaporation equilibrium among the vapor mixture of Si, SiC and C at the top of SiC ingot. Subsequently, the increase of remaining C covering on the surface of ingot will affect the composition of SiC/SiO₂ nanocomposite coating.

3.2. Surface composition analysis of SiC/SiO₂ nanocomposite coating

Before evaporation, molten SiC ingot has been hold 10 min at evaporation temperature to improve the balance among the Si, SiC and C vapor. However, due to the increase of C amount, 10 min holding time is not suitable for every SiC evaporating. Fig. 2 is the relation between evaporation order and the C content at the surface of nanocomposite coating. The C content gradually increases to 0.5 with evaporation order, which results in the increase of evaporation balance time among Si, SiC and C vapor (shown in Fig. 2). However, when C potential in vapor mixture increases to a certain value, a new balance can be achieved in vapor mixture, and C potential does not sequentially increase and gradually reaches a stable value with the increase of evaporation order. Then the C content at the surface of composite coating reaches a maximum of 0.5.

Fig. 3 is the relation between evaporation order and the Si content at the surface of coating. When the amount of Si vapor is sufficient to meet the vapor balance among Si, SiC and C, Si content decreases by conic with the increase of C potential. After several evaporations, C potential sequentially increases. However, the amount of Si vapor is more and more insufficient to meet the vapor balance in 10 min holding time, the vapor mixture trends to achieve another balance, and Si vapor directly reaches substrate under the deviation of vapor balance. Then the Si content at the surface of coating increases with the increase of evaporation order until next vapor balance. This phenomenon sustains to the vapor mixture reaching a new balance. As shown in Fig. 3.

The relation between evaporation order and SiC content at the surface of coating is shown in Fig. 4. Different with that of

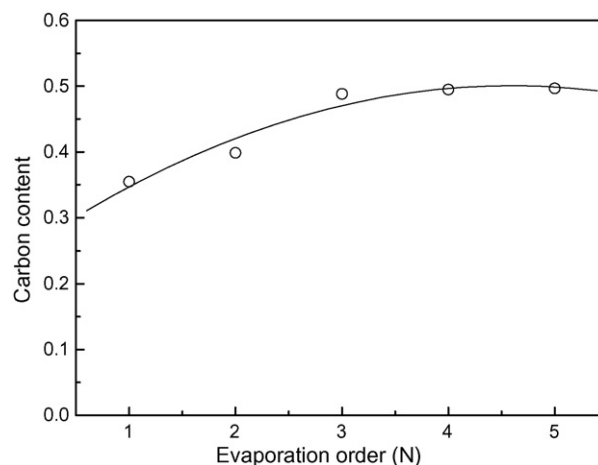


Fig. 2. C content in SiC/SiO₂ nanocomposite coating as a function of evaporation order.

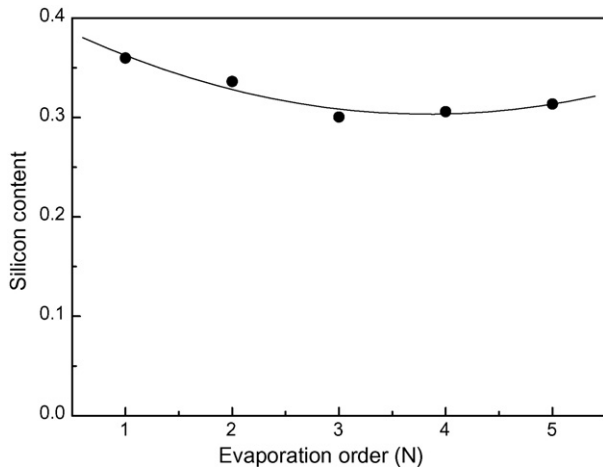


Fig. 3. Si content in SiC/SiO₂ nanocomposite coating as a function of evaporation order.

Si and C, SiC content changes with evaporation order by cubic curve. The minimum of SiC content is not corresponding with the minimum of Si content. With the increase of remaining C, Si content at the surface of coating gradually decreases, and the SiC content also decreases. Before Si content decreasing to minimum, the vapor mixture at the top of ingot has trended to achieve new balance. Then SiC content reaches a minimum. When vapor mixture achieves a new balance, SiC content also reaches a new maximum. However, due to the increase of C potential in vapor mixture, the new maximum of SiC content is a little less than previous maximum. With the increase of evaporation times, the vapor mixture continuously achieves a new balance and the maximum content of SiC finally trends to be equal with the minimum content of it in SiC/SiO₂ nanocomposite coating. As shown in Fig. 4.

3.3. XPS depth profile analysis of SiC/SiO₂ nanocomposite coating

Figs. 5 and 6 are XPS depth profiles of SiC/SiO₂ nanocomposite coating of first and last evaporation, respec-

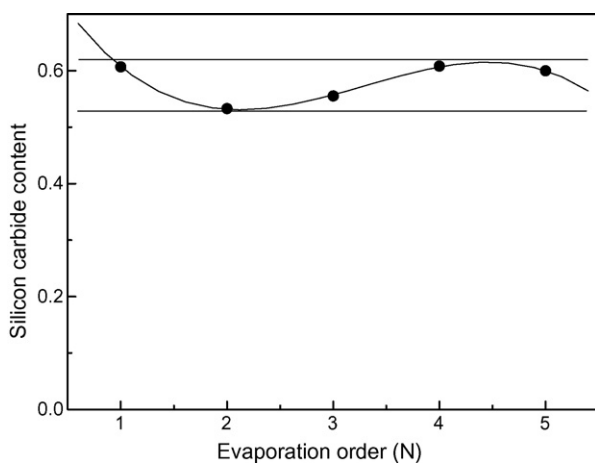


Fig. 4. SiC content in SiC/SiO₂ nanocomposite coating as a function of evaporation order.

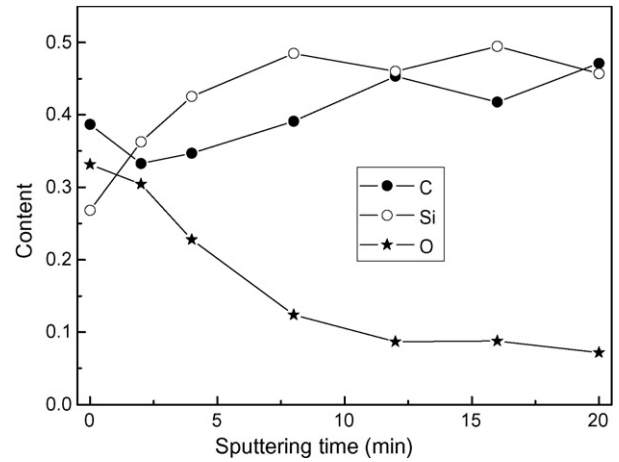


Fig. 5. XPS depth profile analysis of SiC/SiO₂ nanocomposite coating of first evaporation.

tively. The ratio of C/Si is closed to 1 except that at the surface of coating, and C at the surface of coating is partially due to the absorption of impurity carbon (shown in Fig. 5). Although the content of C is larger than that of Si in 40 min sputtering time, the contents of C and Si still trend to be equal (shown in Fig. 6). The results from Figs. 5 and 6 are consistent with the results of Figs. 2 and 3. Moreover, although the reuse of SiC ingot has an effect on the composition of SiC/SiO₂ nanocomposite coating, the effect is not large and acceptable.

3.4. Nanoindentation analysis of SiC/SiO₂ nanocomposite coating

The hardness of SiC/SiO₂ nanocomposite coating is measured by nanoindentation (shown in Fig. 7). The hardness of SiC/SiO₂ nanocomposite coating decreases with the increases of evaporation order, which is due to the increases of graphite C in composite film. Moreover, the hardness of the first evaporation is closed to the results of Kulikovskiy et al. [10]. The reason is that nanocrystal in coating improves the hardness of SiC/SiO₂ nanocomposite coating.

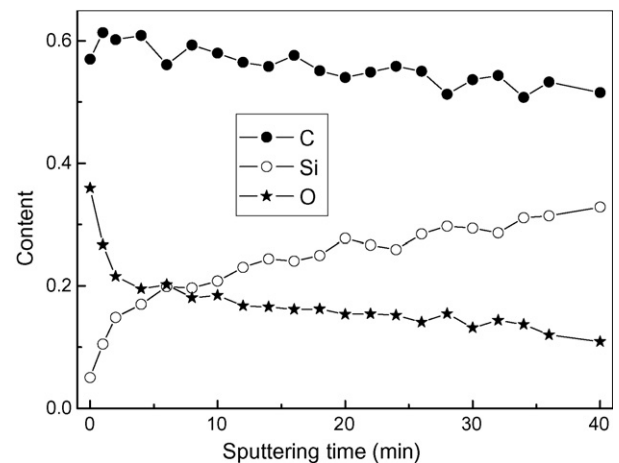


Fig. 6. XPS depth profile analysis of SiC/SiO₂ nanocomposite coating of last evaporation.

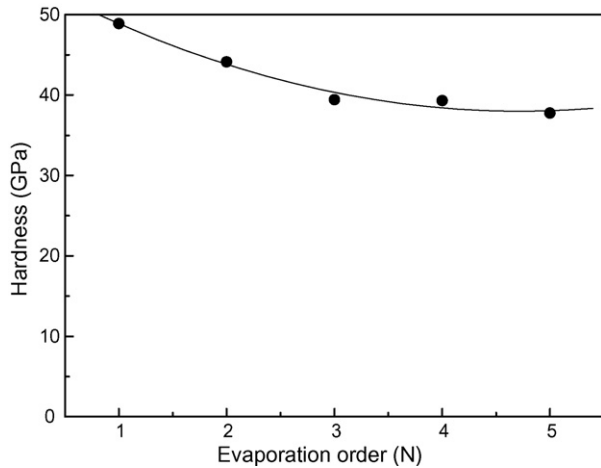


Fig. 7. Nanohardness of SiC/SiO₂ nanocomposite coating as a function of evaporation order.

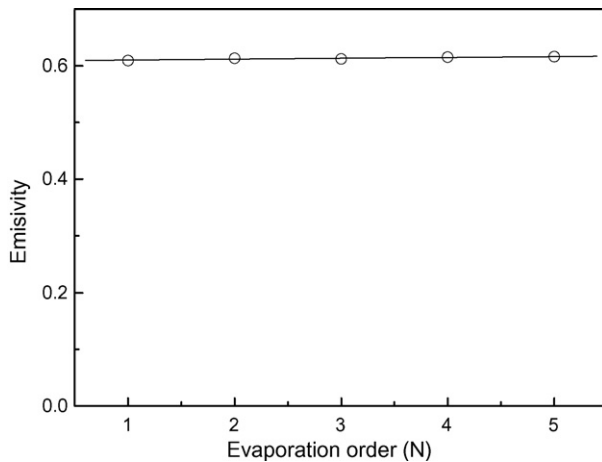


Fig. 8. Average spectral normal emissivity SiC/SiO₂ nanocomposite coating as a function of evaporation order.

3.5. The emissivity of SiC/SiO₂ nanocomposite coating

The relation between the average spectral normal emissivity and evaporation order is shown in Fig. 8. The average spectral normal emissivity of these five coatings sample hardly changes. Among the bonds of C–C, C–Si (Si–C) and Si–Si, the C–C bond has the highest emissivity of 0.95 and C–Si has the second highest emissivity of 0.90. In addition, the total content of C–C and C–Si is larger than 0.9 in the SiC/SiO₂ composite coating. As a result, the influence of surface components on the emissivity of SiC/SiO₂ nanocomposite coating mainly depends on the total content of C–C (C–C %) and C–Si (C–Si %) bonds. Because the total contents of C–C and C–Si bonds are almost

the same, so the average spectral normal emissivity of all five films is similar. As shown in Fig. 8.

4. Conclusions

During EB-PVD preparing SiC/SiO₂ nanocomposite coating through depositing SiC target on pre-oxidized SS substrate, a quantity of analytical C remained and covered on the surface of SiC ingot, which had an effect on the composition, hardness and emissivity of coating. With the increase of evaporation times, C concentration gradually increased to a maximum value of 0.5. However, Si concentration gradually decreased to a minimum value and then increases to a new maximum value. SiC concentration changes with the increase of evaporation times by cubic curve. Moreover, SiC concentration in different SiC/SiO₂ nanocomposite coating finally trends to be equal with the increase of evaporation times.

Although the hardness of SiC/SiO₂ nanocomposite coating gradually decreases and trends to be stable with the increases of evaporation times, spectral normal emissivity of composite coating scarcely fluctuate. It is suitable to prepare SiC/SiO₂ high emissivity nanocomposite coating using reused ingot by EB-PVD.

Acknowledgements

This project was supported by the New Century Excellent Talents Plan of china (NCET2004) and the National Natural Science Foundation of China (50304007).

References

- [1] A. Ordine, C.A. Achete, O.R. Mattosa, I.C.P. Margarit, S.S. Camargo Jr., T. Hirsch, Surf. Coat. Technol. 133–134 (2000) 583.
- [2] S. Ulrich, T. Theel, J. Schwan, V. Batori, M. Scheib, H. Ehrhardt, Diam. Relat. Mater. 6 (1997) 645.
- [3] S.K. Gong, H.B. Xu, Q.H. Yu, C.G. Zhou, Surf. Coat. Technol. 130 (2000) 128.
- [4] A.K. Costa, S.S. Camargo Jr., C.A. Achete, R. Carius, Thin Solid Films 377–378 (2000) 243.
- [5] Z.Q. Fu, C.h. Tang, T.X. Liang, R.J. Charles, Nucl. Eng. Des. 234 (2004) 45.
- [6] H. Kobayashi, T. Sakurai, M. Takahashi, Y. Nishioka, Phys. Rev. B 67 (2003) 115305.
- [7] G.V. Soares, C. Radtke, I.J.R. Baumvol, F.C. Stedile, Appl. Phys. Lett. 88 (2006) 041901.
- [8] B.A. Movchan, G.S. Marinski, Surf. Coat. Technol. 100–101 (1998) 309.
- [9] B.A. Movchan, Surf. Coat. Technol. 149 (2002) 252.
- [10] V. Kulikovskiy, P. Boháč, J. Zemek, V. Vorlíček, A. Kurdyumov, L. Jastrabík, Diam. Relat. Mater. 16 (2007) 167.