Journal of the European Ceramic Society 21 (2001) 87–91
www.elsevier.com/locate/jeurceramsoc

Young's modulus and residual stress of plasma-sprayed boron carbide coatings

Yi Zeng [a,*], Chuanxian Ding [a], Soo W. Lee [b]

[a] *Shanghai Institute of Ceramics, Chinese Academy of Science, Shanghai, PR China*
[b] *Department of Materials Engineering, Sun Moon University, South Korea*

Received 28 January 1999; received in revised form 10 May 2000; accepted 26 May 2000

Abstract

This paper addresses the application of nondestructive evaluation techniques, such as the use of ultrasonic and X-ray techniques, for characterizing the quality of plasma-sprayed boron carbide coatings. The Young's modulus and shear modulus of plasma-sprayed boron carbide coatings were measured by an ultrasonic echo technique. The residual stresses of coatings were determined by X-ray diffraction technique. The relationship between Young's modulus and microstructure of the coatings is discussed. The results showed that the spraying distance has a significant effect on the phase composition and microstructure of boron carbide coatings. The elastic modulus of boron carbide coatings decreases with increasing spraying distance. This is explained by the increasing content of B_2O_3 and pores in the boron carbide coatings. The residual stresses of the coatings show a polynomial relationship with the spraying distance.

Keywords: B_4C; Elastic modulus; Plasma spraying; Residual stress

1. Introduction

Boron carbide is a kind of ceramics with a high microhardness and high Young's modulus. It makes B_4C coatings good for wearing parts.[1] Also, B_4C coating is utilized significantly in nuclear fusion plants for its excellent resistance to thermal shock and good stability with respect to fusion plasma erosion.[2,3] These achievements can be influenced by the materials–property mismatch between the coating and the substrate. For example, a mismatch in the thermal expansion coefficient and the elastic modulus results in residual stress, which may cause bending, microcracking, spalling, and delamination.[4] To extend the knowledge of the properties of boron carbide coatings, the residual stress and the elastic modulus should be investigated. Most of the measurements of residual stress and elastic modulus applied on the plasma-sprayed coatings are destructive and must be performed on thick test samples made of the same materials. Nondestructive testing methods, such as the ultrasonic[5] and X-ray diffraction techniques,[6,7] can be applied to the coated workpiece. This paper focuses on the application of advance sensing and quality characterization techniques, based on emerging nondestructive evaluation (NDE) methods to assess product quality at various stages of plasma-sprayed boron carbide coatings. The development of such techniques is critical because they provide valuable information on the relationship between process variables and product properties. Elastic behavior and residual stress of the boron carbide coatings is important in quality characterization. Young's modulus, shear modulus and Poisson's ratio as a function of sprayed distance are required as inputs to process models of manufacturing processes. These properties can also be used as quality control parameters, i.e. as a measure of the process quality.

* Corresponding author.
E-mail address: zyidq_2000@yahoo.com (Y. Zeng).

2. Experiment

The specimens were produced by atmospheric plasma spraying (APS-Plasma Technik System, Wohlen, Switzerland) on stainless steel substrates that have been sandblasted with corundum. A commercial boron carbide powder was used as the feedstock. All the coating thickness was about 200 μm.

0955-2219/01/$ - see front matter
PII: S0955-2219(00)00169-2

X-ray photoelectron spectroscopy (XPS) analysis was used to determine the type of phase present in the as-sprayed coatings. Scanning electron microscopy (SEM) was used to observe the as-sprayed coating structure.

The ultrasonic pulse echo technique with glycerine as the ultrasound coupling medium was used to characterize the above coatings. The schema of the technique is shown in Fig. 1. Wave velocities were calculated by dividing travel distance by the time difference between echoes e2 and e3. Longitudinal wave velocity was measured at 50 MHz frequency, and the shear wave velocity was measured at 100 MHz frequency. Transit time of flight measurements to 1 ns resolution was performed utilizing a Lecroy 9420 digital storage oscilloscope.

The residual stresses of boron carbide coatings were measured by the well known $\sin^2\psi$ method,[7] using Siemens D500-diffractometer with Ni-filtered Cu radiation. Reflection from (119) crystal planes was used, with 2θ 139°. Strain values from these reflections were then converted to stresses.

3. Results and discussion

3.1. XPS analysis

Overview XPS spectra from the boron carbide coatings reveals in addition to peaks from B, O and C, only small peak from Fe. The Fe peak may be the impurity in the starting boron carbide powder. The B_{1s} peak of a particular XPS spectrum of coating with 80 mm sprayed distance could be analysed as three components. The major part of boron is present as B_4C as shown in Fig. 2(a). The high binding energy B_{1s} peaks at 190.3 and 192.3 ev can be assigned to the low valance B_xC. The B_{1s} peaks at 193.3 ev arise when the spraying distance increases to 100 mm, as shown in Fig. 2(b), which refers to the oxidation of boron carbide powder during the plasma process. The B_{1s} peak at 193.3 ev becomes more pronounced, which indicates that the oxidation of boron carbide powder is more significant when the spraying distance increases to 120 mm [Fig. 2(c)]. Table 1 gives the content of B_2O_3 phase in the coatings calculated from the XPS spectrum. It can be seen that the degree of oxidation of boron carbide increased with the increase of sprayed distance.

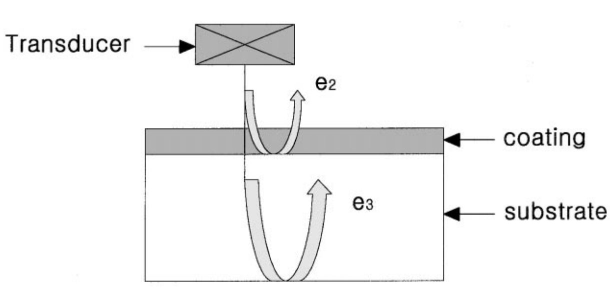

Fig. 1. The pulse echo technique investigation schematic diagram.

3.2. SEM analysis

The microstructure of B_4C coatings with different spraying distances is shown in Fig. 3. From Fig. 3, it can be seen that the pores and their distribution as well as the melted state of B_4C particles were different at different spraying distance. The coating with spraying distance 80 mm is the most dense and even, and with the increase of spraying distance, the pores of B_4C coating increase. It could be accounted for by two reasons. One is that the starting powder would be more easily oxidized with increasing spraying distance, which has been

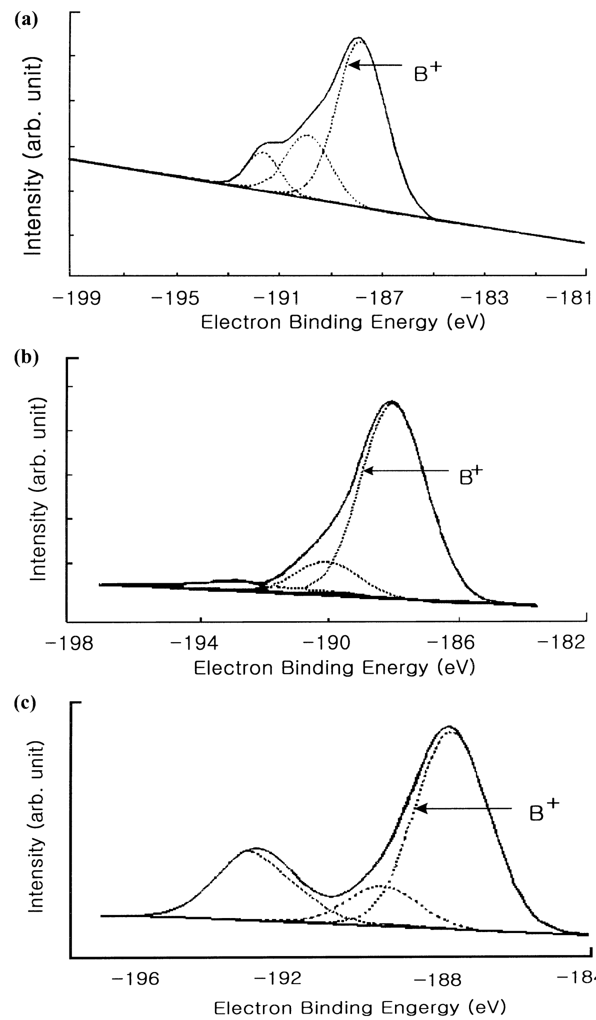

Fig. 2. XPS spectrum of boron carbide coatings at different sprayed distance: (a) 80; (b) 100 and (c) 140 mm.

Table 1
The content of B_2O_3 phase in the coatings

	Sprayed distance (mm)				
Content (%)	80	100	120	140	160
B_2O_3 phase	0	4	7	14	16

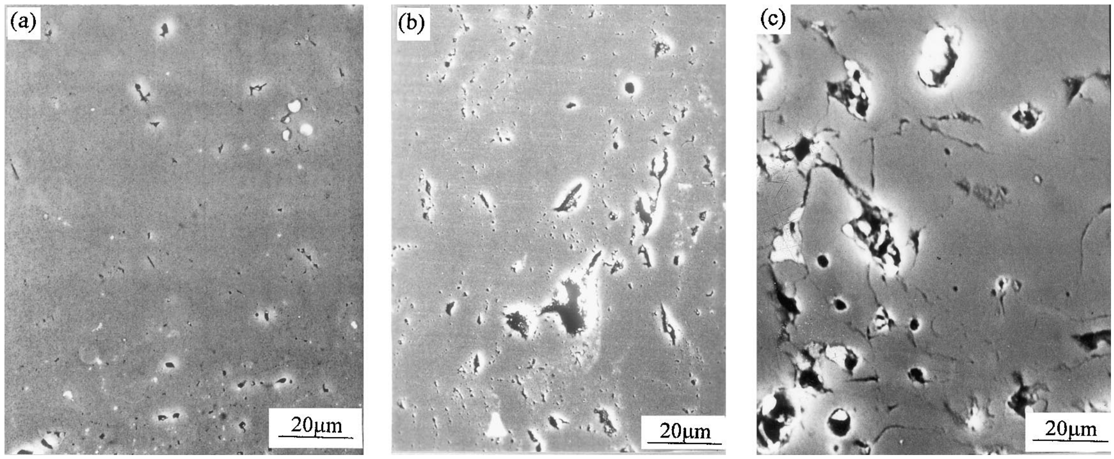

Fig. 3. Microstructure of boron carbide coatings at different sprayed distance: (a) 80; (b) 100 and (c) 140 mm.

proved by the results of XPS results. The gas produced by oxidation of B_4C powders is wrapped in the melted particles and developed the pores in the coating. The other reason may be that the temperature of B_4C particles became lower when the spraying distance became longer. It would result in the loose contact between the layers of coatings. Table 2 gives the porosity of boron carbide coatings with different sprayed distances. It agrees with the results observed in Fig. 3.

3.3. Ultrasonic measurements

Ultrasonic pulse echo technique was used to determine elastic properties of plasma-sprayed boron carbide coatings. More detailed descriptions are revealed in previous work.[4] The stress–strain behavior, stress field at the interface, surface hardness, etc., of coated systems all depend on the elastic modulus, E, of the coating. As a result, the elastic modulus of the coating is a fundamental parameter for characterizing coating performance. E must be determined to measure residual stress distributions.

If the plasma-sprayed coating is assumed to be isotropic, the velocities of shear and longitudinal waves in the coatings can be used to determine their elastic properties. If V_L and V_T are the velocities of longitudinal and shear waves, respectively, and ρ is the density, then

$$G = \rho VT \tag{1}$$

Table 2
The porosity of boron carbide coatings at different sprayed distance

Sprayed distance (mm)	Porosity (%)
80	4
100	9
120	11
140	19
160	23

$$\nu = \frac{V_L^2 - 2V_L^2}{2\left(V_L^2 - V_T^2\right)} \tag{2}$$

$$E = 2G(1 + \nu) \tag{3}$$

where E is Young's modulus of coating, G is shear modulus of coating, and ν is Poisson's ratio.

The spraying distance dependence of Young's modulus and shear modulus of B_4C coatings is shown in Fig. 4. It can be seen that the B_4C oating with high Young's modulus could be produced by selecting a suitable spraying distance and the Young's modulus tends to decrease as the spraying distance rises. Fig. 5 shows plot of calculated Young's modulus, as function of porosity, in the compressive direction, determined by the ultrasonic technique. It was found that the elastic modulus is very different with that previously reported by Liu et al.,[8] who found that there is the following relationship between modulus and porosity:

$$E = E_0(1 - p)^n \tag{4}$$

where E_0 is the Young's modulus of bulk materials, p is the porosity and n is a permanent.

The different sprayed distances change the porosity and contents of B_2O_3. Under the mutual action of these two factors, the porosity dependence of Young's modulus deviates from the above relationship.

3.4. Residual stress

The spraying distance dependence of residual stress in boron carbide coatings is shown in Fig. 6. It can be seen that the stresses are compressive and show polynomial regulation with the increase of spraying distance. In order to investigate further the effect of spraying distance on the stress, the coatings are annealed in a 400°C furnace for 5 min to reduce the quenching stress. The stress of the coatings after annealing is shown in Fig. 7. The

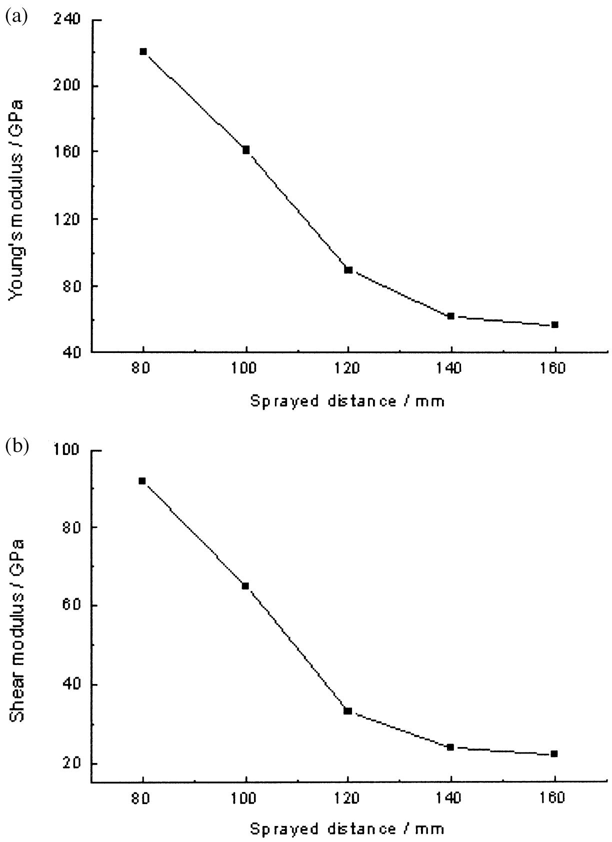

Fig. 4. The elastic modulus of boron carbide coatings at different sprayed distance: (a) Young's modulus and (b) shear modulus.

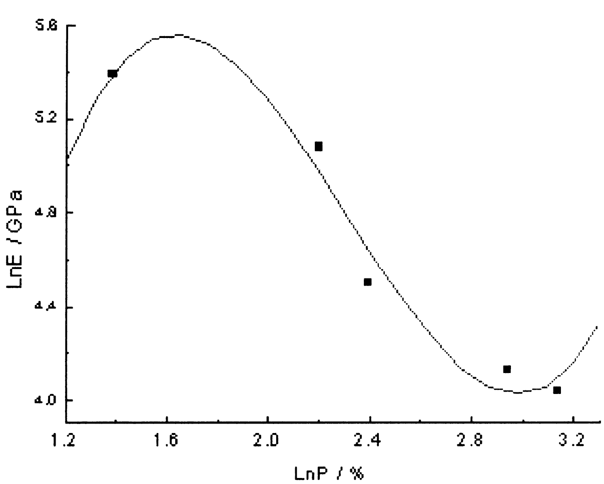

Fig. 5. The dependence of Young's modulus on the porosity of boron carbide coatings.

compressive stress is markedly increased after annealing. It is usual that the stress of coatings will reduce after annealing, but there are opposite phenomena in our experiment.

The composition of stress of coatings could account for it. We can get the following Eq. (5) if elastic behavior and perfect bonding between the coating and the substrate was assumed.

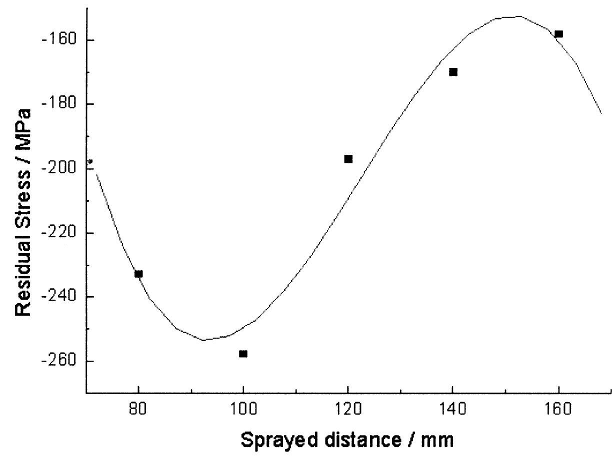

Fig. 6. The dependence of residual stress of boron carbide coatings on the sprayed distance.

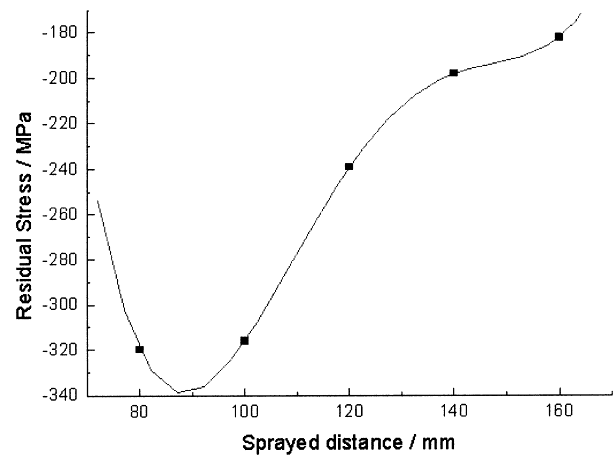

Fig. 7. The dependence of residual stress of boron carbide coatings after annealing on the sprayed distance.

$$\sigma_{RC} = \sigma_{QC} + \sigma_{TC} \quad (5)$$

σ_{RC}, σ_{QC}, σ_{TC} being the residual, quenching and thermal stresses in the coating, respectively.

Also, the thermal stress in this case is compressive, since the thermal expansivity of boron carbide is smaller than that of steel. The stress would mostly be thermal stress after annealing, because the quenching stress is often tensile and after annealing it would decrease obviously according to the work of Matejicek et al.,[9] so the compressive stress would increase after annealing.

4. Conclusion

The spraying distance has significant effect on the phase composition and microstructure of boron carbide coatings. The results of XPS analysis show the extent of oxidation of boron carbide powder is more significant with the increase of sprayed distance. The elastic modulus of boron carbide coatings would decrease along with increasing sprayed distance, which is explained by the contents of B_2O_3 and pores in the coatings. The residual stress of boron carbide coatings shows a near-polynomial relationship with the spraying distance and, after annealing, it would increase.

References

1. Mallener, W. and Stover, D., Plasma spraying of boron carbide using pressures up to two bar. In Proceeding of the 1993 *National Thermal Spray Conference,* Anahelm, CA, 7–11 June 1993, pp. 291–295.
2. Shi, C. X., *Chinese Materials Technology Encyclopedia*. Chinese Scientific Press, Beijing, 1992, p. 841.
3. Zhang, H., Preparation of cross-sections of thermal spray coating for TEM investigation. *Journal of Thermal Spray Technology*, 1992, **1**, 83–88.
4. Chiu, C. C. and Case, E. D., Elastic modulus determination of coatings layers as applied to layered ceramic composites. *Mater. Sci. Eng*., 1991, **132**, 39–47.
5. Vincent, A. and Moughlil, A., Ultrasonic characterization of zirconia based thermal barriers. *NDT Int*., 1989, **22**, 283–291.
6. Richard, C. S., Lu, J., Beranger, G. and Decomps, F., Study of Cr_2O_3 coatings. *Journal of Thermal Spray Technology*, 1995, **4**(4), 342–346.
7. Clyne, T. W. and Gill, S. C., Residual stress in thermal spray coatings and their effect on interracial adhesion: a review of recent work. *Journal of Thermal Spray Technology*, 1996, **5**(4), 401–406.
8. Liu, X. Y., Guo, J. K. and Yan, D. S., Young' modulus of sintering alumina. *Journal of Chinese Inorganic Materials*, 1996, **12**(2), 128–135.
9. Matejicek, J., Sampath, S. and Herman, H., Processing effects on splat formation. microstructure and quenching stress in plasma sprayed coatings. In *Proceeding of the 15th International Thermal Spray Conference,* Nice, France, 25–29 May 1998, pp. 419–424.