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Synthesis and characterization of aluminum oxide–boron carbide coatings by air plasma spraying

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Abstract

Aluminum oxide (Al_2O_3)–boron carbide (B_4C) composites have been proposed for use as cutting tools as well as in high temperature applications due to their high hardness and fracture toughness. The air plasma spraying method was used to fabricate the composite coatings of Al_2O_3 and B_4C. Three different Al_2O_3:B_4C composition ratios of 90:10, 80:20, and 70:30 by weight were plasma sprayed on plain carbon steel substrates. The effect of B_4C content on microstructure, hardness, porosity and thermal diffusivity of the coatings were studied using scanning electron microscopy (SEM), microhardness testing, X-ray diffraction (XRD), and the flash diffusivity method. The plasma spray parameters were optimized in order to achieve a theoretical density of approximately 90%.

Keywords: Air plasma spraying; Alumina; Boron carbide; Thermal diffusivity; Vickers hardness

1. Introduction

Plasma spraying is a relatively new process that is characterized by an ionized gas stream, which can have temperatures in excess of 10,000 °K. The powders are sprayed into the ionized gas stream (plasma) and then accelerated to supersonic speeds to coat the substrate with the powder mixture. This causes the powder to partially or fully melt depending on the thermal properties of the powder. Extremely high heating and cooling rates allow any combination of powders to be sprayed: metals, ceramics, non-metals, and any combinations of the above. This technique has extremely high deposition rates and is ideal for coating large parts with relatively uniform coating thickness.

Alumina (Al_2O_3) and zirconia (ZrO_2) are the most useful among oxide ceramics, owing to ease of fabrication and their high temperature stability [1,2]. In particular, alumina has a great potential for applications due to its high hardness, low cost, corrosion resistance, wear resistance, and high refractoriness [3–7]. For applications involving high temperatures, the oxidation resistance of these oxides makes them a natural choice for materials operating at elevated temperatures in air [1,8,9]. Exposure to high temperature induces large volumetric phase transformations, leading to structural instability. Thermal shock failures are more pronounced in ceramics due to their brittleness. Therefore, toughening the oxide ceramics becomes important in applications involving high temperatures.

Boron carbide (B_4C) is one of the hardest materials known. It ranks third behind diamond and cubic boron nitride. Boron carbide also has low density and good resistance to chemical agents. Most importantly, B_4C provides a good chemical erosion resistance to avoid contamination of the plasma in combination with reasonably good thermal properties [10]. B_4C composites can be applied as a coating material on cutting tools and as protection for a tokamak wall in nuclear fusion [11].

Graded microstructure and incorporation of secondary phases have been used conventionally for the enhancement of fracture toughness in oxide ceramics [12–15]. Alumina has been reinforced by previous researchers using metallic additives such as aluminum [16] and nickel [17]; using ceramic secondary phases such as titania particles [18–20], silicon carbide [21,22], zirconia [23,24], and yttrium aluminum garnet [6] resulting in the enhancement of the fracture toughness of alumina.

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In the present work, three samples with Al_2O_3:B_4C weight percent composition ratios of 90:10, 80:20 and 70:30 were plasma sprayed on the plain carbon steel substrate. The lower density, higher hardness, and higher thermal conductivity of boron carbide, when compared to alumina, can result in decreased weight, increased hardness and higher thermal conductivity of the plasma-sprayed coating when boron carbide is mixed with alumina. The increase of thermal conductivity and hardness makes these types of coatings very attractive for use in nuclear reactors.

2. Materials and methods

FlowMaster™ oxide powder, aluminum oxide (99.5% Al_2O_3, fused/crushed −50/+20 μm particle size 13.8/20–50), and FlowMaster™ carbide powder, boron carbide (99.5% B_4C, fused/crushed −50/+20 μm particle size 5.6/20–50) manufactured by F.J. Brodmann and Co., L.L.C. were used in this research. The powders were mixed in a jar mill (US Stoneware, East Palestine, OH) for 96 h to obtain a uniform mixture of the alumina–boron carbide powders. The samples were designated Sample A (Al_2O_3:B_4C – 90:10 by wt%), Sample B (Al_2O_3:B_4C – 80:20 by wt%), and Sample C (Al_2O_3:B_4C – 70:30 by wt%), respectively.

The alumina–boron carbide coatings were deposited by atmospheric plasma spraying (APS) with a Praxair SG 100 gun onto plain carbon steel substrates. The plain carbon steel substrates were sandblasted prior to plasma spraying.

The plasma spray parameters play a critical role in producing the desired coating properties. Although DC-plasma spraying has been used practically for many years, the process remains highly empirical. The production of coatings is still based on trial-and-error approaches, depending on the experience and the instinctive feeling of the operator. The main reason for this is the lack of understanding of the underlying physical processes during plasma spraying. More than 50 macroscopic parameters influence the quality of a coating [25].

The composite coating formed with boron carbide and alumina requires high temperatures for melting the mixture. Boron carbide requires high temperature for decomposition and/or melting due to its high hardness and high chemical resistance. Previous researchers [26,27] have indicated that spraying boron carbide requires power of the order 50 kW. The current and voltage are therefore selected to produce power in this range to spray the alumina–boron carbide composite coatings. The optimum spraying distance, which results in minimum porosity, is of the order 80 mm [26,27]. The main parameters to obtain clean and non-porous alumina–boron carbide composite coatings using the plasma spray technique are current = 800 A, voltage = 40 V, and primary:secondary:-carrier gas pressure ratios of 40:75:30 psi.

The samples were mounted, cross-sectioned, and polished. Then the microstructure was analyzed using the JEOL JSM 6330F field emission-scanning electron microscope. The porosity of the samples was determined from the scanning electron microscopy (SEM) images using Image-Pro® Plus, Version 5.1 imaging software (2004 Media Cybernetics Inc.). The roughness was determined by using a stylus scanning the surface. XRD spectrum was obtained using Siemens D-500 operating at 40 kV and 20 mA with Cu Kα peak of 1.54 Å. Hardness and fracture toughness of the plasma-sprayed samples were measured with the Vickers indentation technique using the Shanghai Taiming Optical Instruments, Zhongguo, HXD-100 TMC microhardness tester (100 g load and 5 s dwell time). Density of the coatings was analyzed through the Archimedes principle. Thermal diffusivity was measured using the laser flash technique by means of a Microflash 300/RT model instrument (Holometrix Micromet, Bedford, USA) with the necessary in-plane software. The thermal diffusivity measurement of nanocomposites was done with a perpendicular orientation to the sintering direction, which is also referred to herein as the ‘‘in-plane’’ direction. The in-plane thermal diffusivity of samples was measured at different temperatures, ranging from 25 °C to 250 °C.

3. Results and discussion

The samples were designated Sample A (Al_2O_3:B_4C – 90:10 by wt%), Sample B (Al_2O_3:B_4C – 80:20 by wt%), and Sample C (Al_2O_3:B_4C – 70:30 by wt%). Each coating was analyzed for coating thickness, surface roughness, and density. A plasma-sprayed coating of pure Al_2O_3 with the same coating parameters was tested for comparison. The results are shown in Table 1. B_4C was shown to have an effect in reducing the density and the coating thickness of the sprayed parts. This is due to the difference in the melting temperatures of B_4C and Al_2O_3, which results in the formation of increasing partially melted regions with increasing weight percent of B_4C. Porosity also results due to the poor bonding of boron carbide to alumina after plasma spraying. As shown in Table 1, higher wt% ratios of boron carbide lead to an increase in the surface roughness along with a decrease in the coating thickness. This trend is attributed to the incomplete melting of boron carbide when it is present in higher wt% ratios.

Table 1
Density, porosity, coating thickness, and surface roughness.

Sample	wt% B_4C	Av. Vickers hardness number	Density (%theoretical density)	Porosity (%)	Coating thickness (μm)	Surface roughness (μm)
*Al_2O_3	0	714	88	13	350	0.75
A	10	1158	90.5	10	203	1.12
B	20	921	86.7	13	152	1.26
C	30	925	81.4	18.5	127	1.55

* Pure Alumina coatings plasma sprayed with same parameters in previous research.

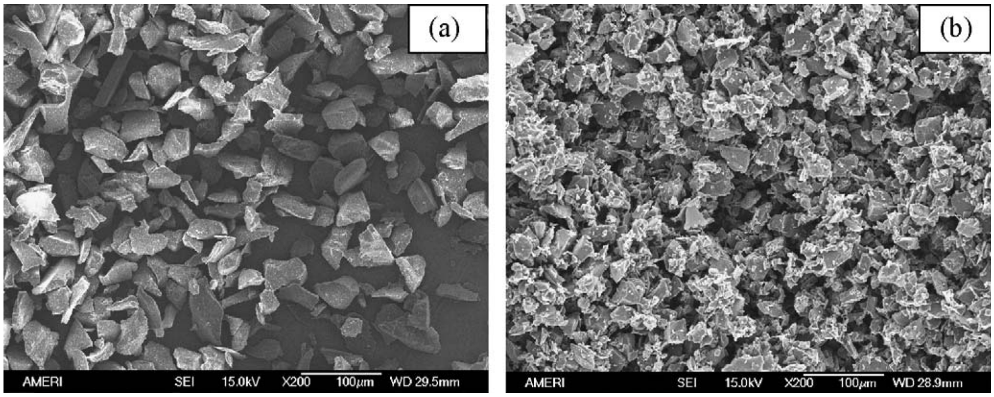

Fig. 1. SEM image of initial powders (a) aluminum oxide and (b) boron carbide.

3.1. Microstructure

The SEM images of cross-sections of the Al_2O_3–B_4C coatings on plain carbon steel substrates are shown in Figs. 1–4. Uniform and homogenous coatings about 100–200 μm thick are obtained. The coatings are free from cracks and adhere well to the substrate. In Sample A (Fig. 2), it is observed that the coating has less porous regions than Sample B (Fig. 3) and Sample C (Fig. 4). Moreover, the B_4C splats are more evenly elongated/spread than Samples B and C. This indicates that a higher degree of melting is obtained in Sample A when compared with B and C. Figs. 2–4 show two distinct regions of partially melted/solid-state sintered regions (PM) and fully melted regions (FM) in the coating. Most of the porosity is observed at the interface of Al_2O_3–B_4C, which is believed to be due to the difference in the coefficient of thermal expansion.

3.2. X-ray diffraction (XRD) analysis

The XRD patterns of the B_4C and Al_2O_3 starting powder along with Sample A (Al_2O_3:B_4C – 90: 10 by wt), Sample B (Al_2O_3:B_4C – 80:20 by wt), and Sample C (Al_2O_3:B_4C – 70:30 by wt) sprayed coatings are shown in Fig. 5. Boron carbide exists in two phases as B_4C and $B_{12}C_2$. The crystal structure of the alumina starting powder was cubic (Al_2O_3) and hexagonal (Al_2O_3). Oxidation of boron carbide to B_6O and B_2O_3 is observed in the coated samples. Alumina retained its two phases, i.e., Al_2O_3 corundum and Al_2O_3 cubic, in the coated samples. No peaks of aluminum carbide or aluminum–boron–carbon com-

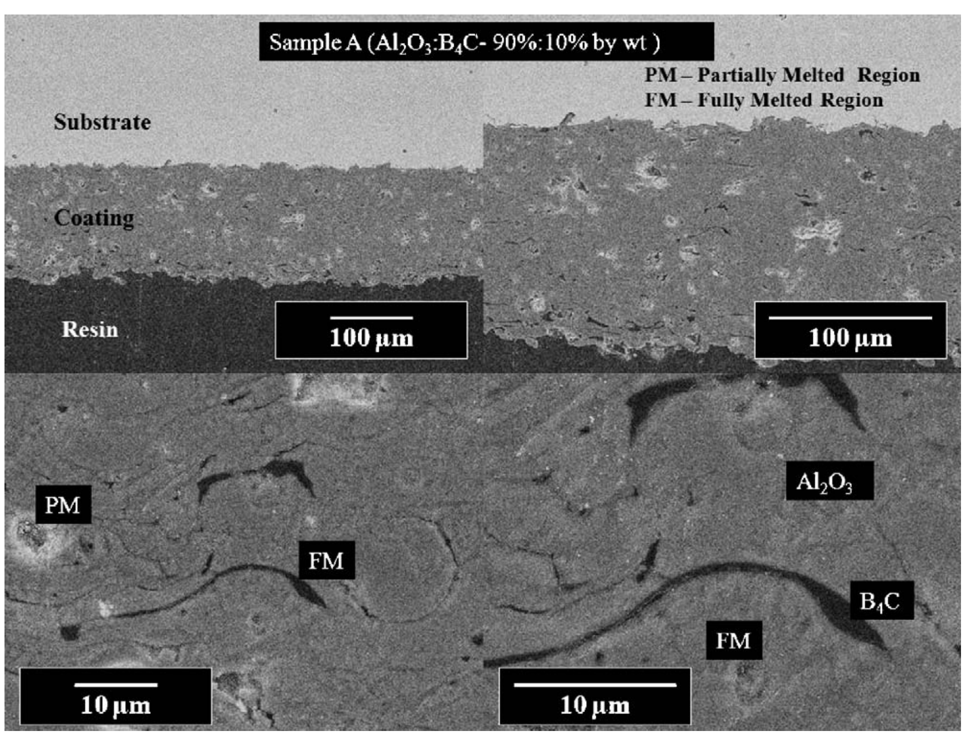

Fig. 2. Microstructure of plasma-sprayed Sample A.

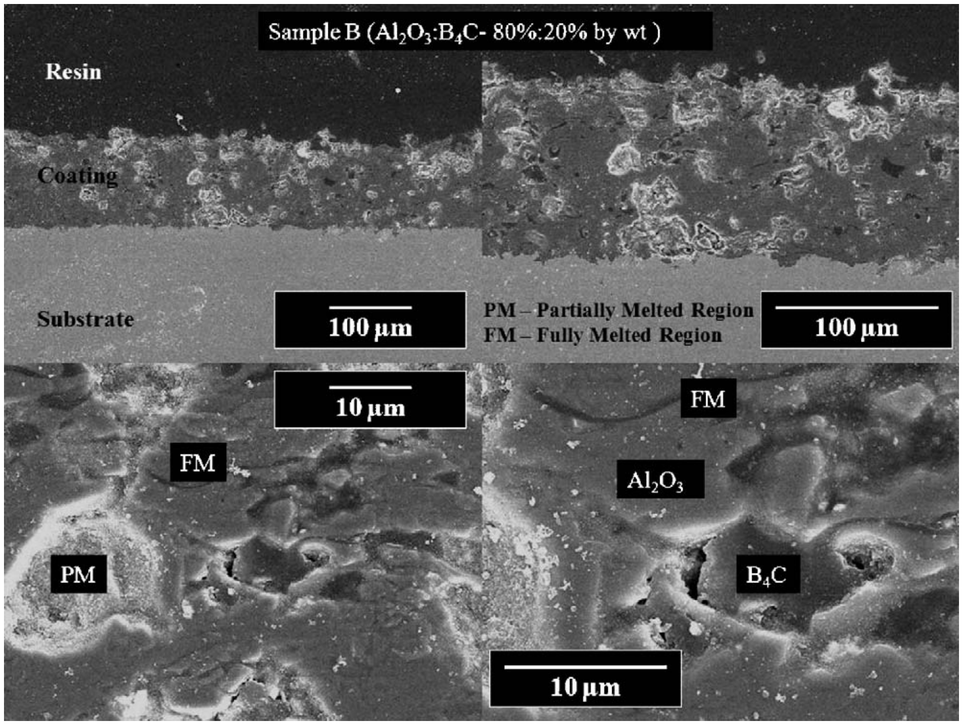

Fig. 3. Microstructure of plasma-sprayed Sample B.

pounds were observed in the coated samples, indicating that there is no chemical reaction between the B_4C and Al_2O_3 particles.

3.3. Microhardness testing

The Vickers hardness testing results are shown in Fig. 6. Microhardness of the plasma-sprayed unreinforced Al_2O_3 was 714.2 V_H. Samples A, B and C demonstrated hardness of 1158 V_H, 921 V_H, and 925 V_H, respectively. These results show that the hardness increases with the addition of boron carbide for Samples A, B, and C, when compared to the pure alumina sample. Sample A has the highest Vickers hardness when compared with Samples B and C, due to the increase in porosity of Samples B and C.

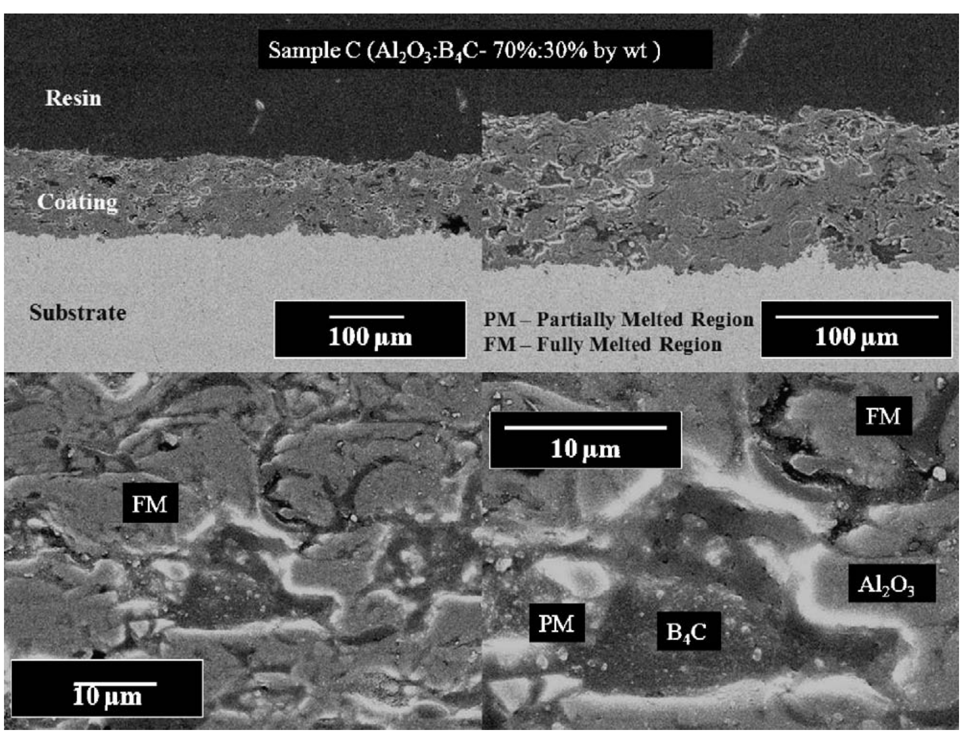

Fig. 4. Microstructure of plasma-sprayed Sample C.

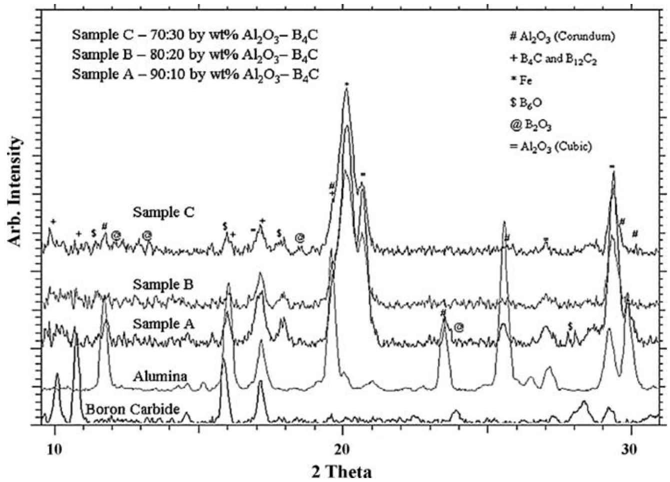

Fig. 5. XRD analysis of coatings.

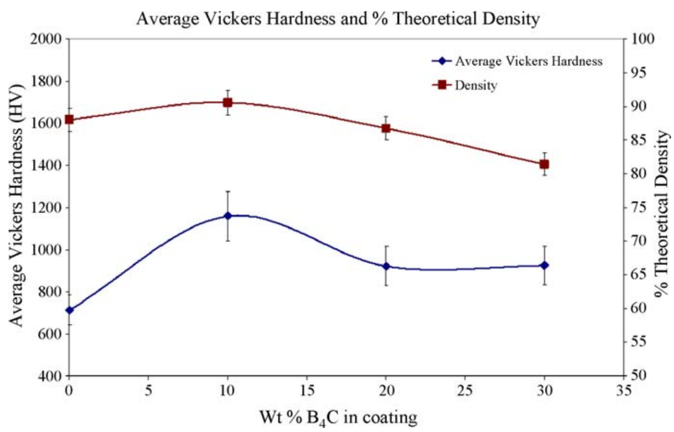

Fig. 6. Vickers hardness testing.

There is no significant variation in the hardness values of Samples B and C.

3.4. Thermal property measurements

B_4C has higher thermal diffusivity than Al_2O_3. It is expected that the thermal diffusivity of the coatings will rise with an increase in the weight percent of B_4C in the original powder mixture. The results of the thermal diffusivity measurements are shown in Fig. 7. It is interesting to note that, even with an increase in the porosity of the samples with a greater weight percentage of boron carbide in the powder mixture, the thermal diffusivity still increases. This indicates that the boron carbide has a more dominant effect in the thermal diffusivity of the sample than the induced porosity caused by the addition of boron carbide.

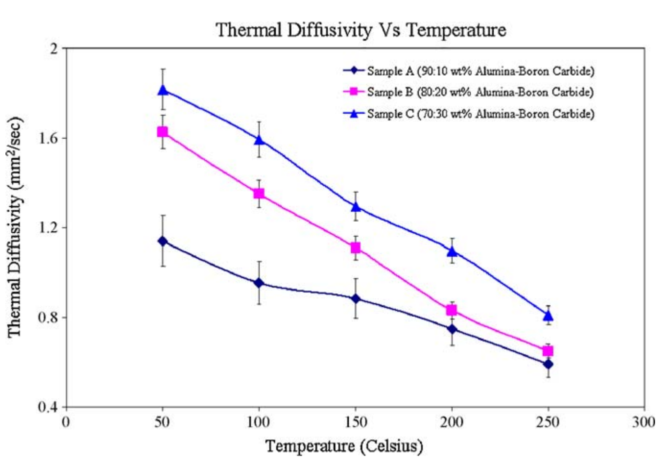

Fig. 7. Thermal diffusivity of Samples A, B, and C.

4. Conclusions

Plasma spraying has been successfully utilized to fabricate Al_2O_3:B_4C (90:10, 80:20, and 70:30 wt%) coatings. Hardness of the coatings increased when compared with the pure alumina. Higher weight percentage of the boron carbide results in higher porosity due to the poor melting of boron carbide. Most of the porous region is accumulated around boron carbide. XRD analysis showed that there is no chemical reaction between boron carbide and alumina. Boron carbide and alumina retained their initial phases as powders. The results show that coatings made with an addition of 10% boron carbide by weight are better in mechanical and thermal properties when compared to pure alumina, especially for applications involving walls of nuclear reactors.

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