

Fly ash cenospheres coatings by EPD-microwave sintering process for SiC corrosion resistance

Alejandra Chávez-Valdez^{1a}, Gregorio Vargas-Gutiérrez^{1b}, José M. Almanza-Robles^{1c}, Ana Arizmendi-Morquecho^{2d}

¹Cinvestav-Unidad Saltillo, Carr. Saltillo-Mty, Km 13.5, A. P. 663, 25000 Saltillo, Coah. México

²Cimav-Monterrey, Autopista Mty-Aeropuerto Km 10. C.P. 66600 Apodaca, N.L. México

^aalejandra.chavez@cinvestav.edu.mx, ^bgregorio.vargas@cinvestav.edu.mx,
^cmanuel.almanza@cinvestav.edu.mx, ^dana.arizmendi@cimav.edu.mx

Keywords: fly ash, cenospheres, EPD, SiC, EBC.

Abstract

Fly ash cenospheres coatings are a promising material in improving the oxidation and corrosion resistance of SiC. In this work, fly ash cenospheres coatings were deposited on SiC substrates by electrophoretic deposition process at 500 V during 30 seconds, 1, 2 and 3 minutes. These coatings were characterized by SEM to observe the surface morphology. The coatings were sintered at 1000, 1100 and 1200°C during 3 hours by microwave heating. After sintering, the coatings were characterized by XRD. Cross sections of the substrate/coating samples were analyzed by SEM/EDS. The coatings with the best deposition and sintering conditions were evaluated by oxidation and hot corrosion resistance tests. The oxidation test was performed in air at temperatures from 1000 to 1300°C during 100 hours. In addition, fly ash cenospheres coatings on SiC and uncoated SiC substrates were subjected to a hot corrosion test at 1000°C during 100 hours in Na₂SO₄. The coatings showed good adhesion after sintering; the main phases of the coating were mullite and SiO₂. The uncoated substrates were found to gain weight due to the formation of SiO₂ at the surface. In contrast, SiC samples coated with fly ash cenospheres showed no weight gain and exhibited no signs of cracking or spallation following the oxidation tests. After the high temperature corrosion test in Na₂SO₄, the uncoated SiC showed signs of oxidation and corrosion while the coated remained unreacted in the presence of molten Na₂SO₄, indicating that the electrophoretic deposition fly ash cenospheres acted as a hot corrosion barrier for SiC substrates.

Introduction

High temperature applications such as turbine components and heat exchangers require the use of silicon based ceramics such as SiC and Si₃N₄ due to their high strength at high temperature. These ceramics depend on a thin silica layer for their effective protection in oxidizing atmospheres. However, the damage of this layer result in rapid degradation [1,2]. Thus, the use of protective environmental barrier coatings (EBC) in these harsh environments becomes a primary necessity. EBC's have been developed to protect silicon carbide components in gas turbine engines from high-temperature environmental attack [3,4]. The future EBC systems must be designed for both thermal and environmental protection of the engine components in combustion gases. In particular, the thermal barrier functions of EBC's are to reduce the component thermal loads and chemical reaction rates, maintaining the required mechanical properties and durability of the component. Environmental barrier coatings have several requirements [4]. The surface of the coating needs to be environmentally resistant against the atmospheres it is exposed to. The coating has to act as an effective diffusion barrier, and must be mechanically tough and free of cracks in order to prevent exposure of the substrate to the environment. The coating should match the thermal expansion coefficient of the substrate to minimize thermal stresses during thermal cycling. And finally, the coating should have a good chemical compatibility with the substrate to reach a good bonding at the interface. Among the materials that can be applied as protective coatings, fly ash is an alternative because it contains hollow glassy microspheres called cenospheres [5] that have low density, low water absorption and low thermal conductivity [6]. Also, the main component of fly ash, mullite

($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$), is a promising coating material for silicon-based ceramics due to its excellent corrosion resistance, creep resistance and high temperature strength. Mullite has a better CTE ($5.7 \times 10^{-6}/^\circ\text{C}$) match with SiC [7].

A variety of processes to apply coatings on SiC ceramics substrates are well known. The EPD process has several advantages such as low cost, uniformity of deposition even for complex and large forms, thickness control of the deposit and simplicity of operation [8,9]. However, it requires a thermal treatment. Thermal treatments by microwave sintering have significant advantages over conventional sintering such as substantial energy savings, very rapid heating rates, reduced cycle time and improved mechanical properties [10].

Experimental

The material used in this work was fly ash obtained from a Mexican carboelectric plant. This material was prepared by sieving through #400 mesh and the substrates used were Hexoloy® SA SiC. The suspensions for electrophoretic deposition were made using acetone as dispersing media and a concentration of fly ash cenospheres of 5 g/l. The pH of the suspension was modified adding NaOH (1 M) in order to increase the mobility of the particles and the zeta potential. Fly ash cenospheres were deposited on SiC at 500 V during 30 seconds, 1, 2 and 3 minutes by electrophoretic deposition. The coatings were sintered at 1000, 1100 and 1200°C during 3 hours by microwaves using a hybrid heating. The use of microwaves volumetrically heat the ceramic from within and an external heating provided by susceptors can help reduce the thermal gradients within the material [11]. The surface and the cross section of the coatings were analyzed by SEM Phillips model XL30 and ESEM equipped with EDXS. The evaluation of the substrates with and without coating was carried out by oxidation tests from 1000 to 1300°C during 100 hours in order to evaluate the protection of the same. These tests were done in a Thermolyne furnace with a heating rate of 5°C/min. The hot corrosion test was done putting the coatings and substrates in a sealed alumina crucible in presence of Na_2SO_4 at 1000°C during 100 hours. Finally, the phases present in the coatings were evaluated using a Philips X-Pert PW 3040 diffraction unit, attached with secondary monochromator. The instrument was run at step scan mode with step size ($0.05^\circ(2\theta)$) and 5 s time per step, with 2θ angle from 10° to 80° .

Results

Fig. 1 shows the photomicrographs obtained by SEM from the surface of the electrophoretic deposition coatings. The surface of the coatings is composed of spheres of 1 to 10 microns. As deposition time increases thicker deposits can be obtained and the amount of agglomerates of bigger size increases. All the coatings presented good adhesion to the substrates. The composition of these coatings has high concentration of oxygen coming from oxides of various elements such as Al, Si, Mg, Ti, Ca and Fe.

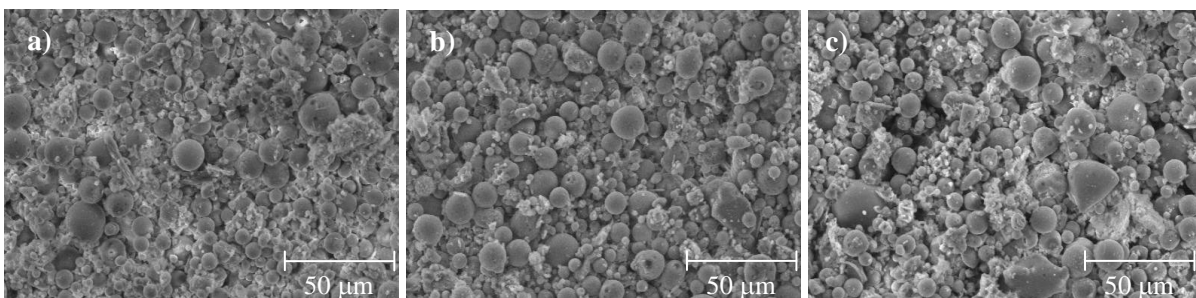


Fig. 1. Surface of fly ash cenospheres coatings obtained at 500 V and 1(a), 2(b) and 3(c) minutes by EPD.

Fig. 2 shows the yield of deposition and the change in electric current of fly ash cenospheres as a function of deposition time. It can be seen that when the applied voltage is constant, time has an

important effect on the deposited mass. As time increases, the deposition mass also increase, however, the relation between time and deposition mass is nonlinear. This can be attributed to a higher specific resistance of the deposit compared with the suspension [12-14]. In the suspension the movement of particles contributes to the conductivity and in the deposit the particles are immobile and therefore do not contribute to the conductivity [15].

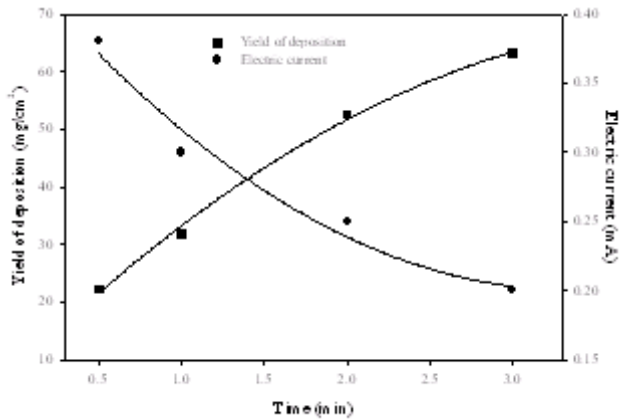


Fig. 2. Yield of deposition and electric current change as function of deposition time.

Fig. 3 shows the SEM images of the sintered coatings. It can be seen a rearrangement of particles in the coating sintered at 1000°C, however, the temperature used was not high enough to reach the sintering of the coating. This coating has a homogeneous surface formed by cenospheres of different sizes. At 1100°C agglomerates of different sizes and necks are formed between particles of the coating. At 1200°C it can be seen a homogeneous and sintered coating which is formed by cenospheres within a sintered matrix and some porosity. Fig. 4 shows the X-ray diffraction patterns of the sintered coatings. At 1000°C the main phases of the coating are mullite, quartz and high cristobalite. By increasing the temperature to 1100°C, more quantity of quartz transforms to high cristobalite. At 1200°C the main phases of the coating are cristobalite and mullite.

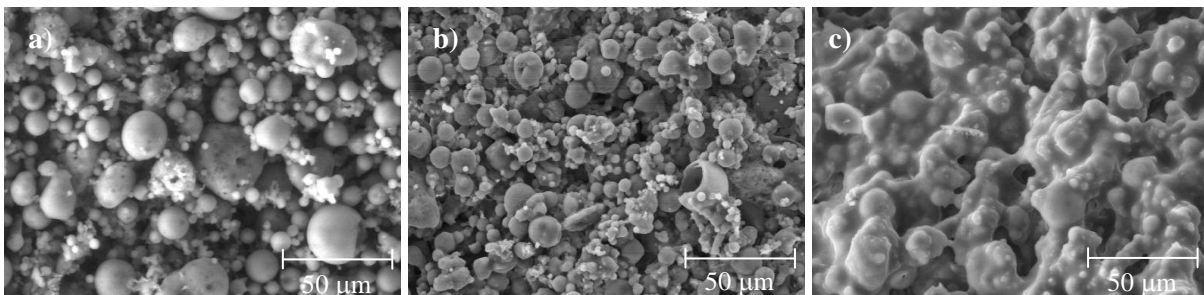


Fig. 3. SEM photomicrographs of coatings surface obtained by EPD at 500 V after 1 minute and sintered by microwaves at (a) 1000°C, (b) 1100°C and (c) 1200°C during 3 hours.

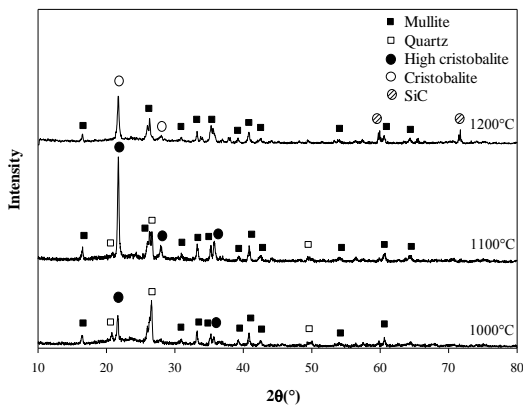


Fig. 4. XRD patterns of sintered fly ash cenospheres coatings.

Fig. 5 shows the photomicrographs obtained by SEM of the surface of the coatings sintered and exposed to oxidation and corrosion tests. The coating sintered at 1200°C shows a well sintered surface which is formed by cenospheres within a sintered matrix and some porosity. After the oxidation test at 1200°C the degree of porosity is reduced considerably and a further degree of sintering is reached. During the oxidation test at 1300°C, an enormous difference occurs due to the change in shape of the coating to a needle like morphology typical of mullite, but in general the coating exposed to oxidation tests acted as an oxidation barrier. The coating exposed to corrosion test at 1000°C has a slight change in the surface but in general seems unreacted in the presence of molten Na_2SO_4 , indicating that the cenospheres coating acted as a hot corrosion barrier.

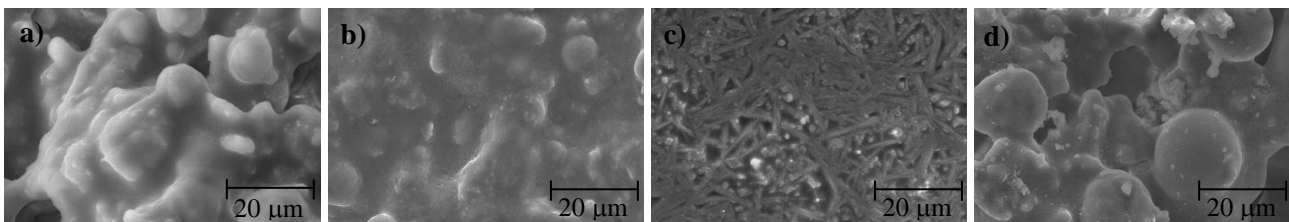


Fig. 5. SEM photomicrographs of coating sintered at 1200°C (a), exposed to oxidation tests at 1200°C during 100 hours (b), exposed to oxidation test at 1300°C during 100 hours (c) and exposed to corrosion test at 1000°C during 100 hours in Na_2SO_4 (d).

Fig. 6 shows the surface of the SiC substrate at different conditions for comparison purposes. It can be seen the surface of the SiC substrate before any treatment and then the substrates exposed to oxidation tests at 1200 and 1300°C during 100 hours. In air tests, the silicon carbide oxidized to form a silica layer, as evidenced by the oxygen content of the surface regions of the air-exposed specimens as seen in the spectrums. Apparently, the oxidation at 1200 and 1300°C causes some form of corrosion on the surface of the substrate. The hot corrosion test of the SiC substrate presents evidence of attack on the surface region. The silica scale formed by oxidation of SiC can react with Na_2SO_4 to form a liquid phase, exposing the surface of the non-reacted SiC to further oxidation [16]. Corrosion affects the lifetime of a material under service not only through the loss of material, but also through the variation of the strength of the material.

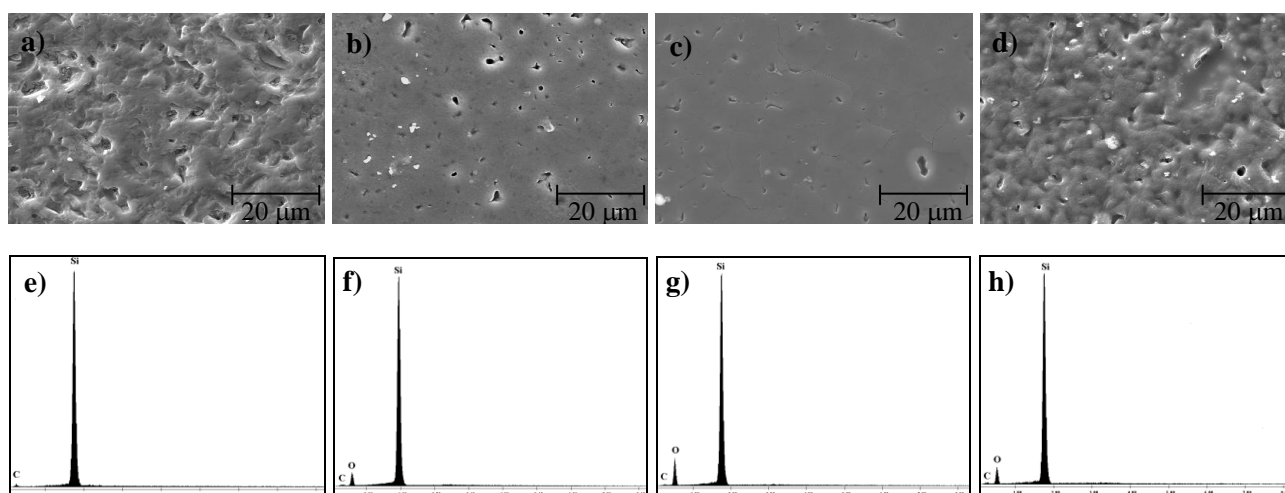


Fig. 6. SEM photomicrographs of the substrate before treatment and spectrum (a,e), after oxidation test and their spectrums at 1200°C (b,f) and 1300°C (c,g) and after corrosion test and spectrum (d,h).

Fig. 7 shows the cross section morphology of the coating after the corrosion test at 1000°C in Na_2SO_4 , with its concentration profile and the cross section of the substrate exposed to oxidation tests at 1300°C. It is important to observe that none of the coatings showed cracks or spallation during the oxidation and corrosion tests which give them a great probability to use them as protective coatings. The concentration profile of Na and Mg indicate that there was no diffusion of these elements to the substrate as shown in the beginning of the concentration profile and that they are present at approximately 75 microns in the zone of the coating. As it can be seen, the cross section of the substrate exposed to oxidation test at 1300°C showed weight gain due to the formation of SiO_2 at the surface, which was easily removed exposing the substrate to further oxidation. The rate of oxidation is generally influenced by the porosity of the material and the exposure temperature.

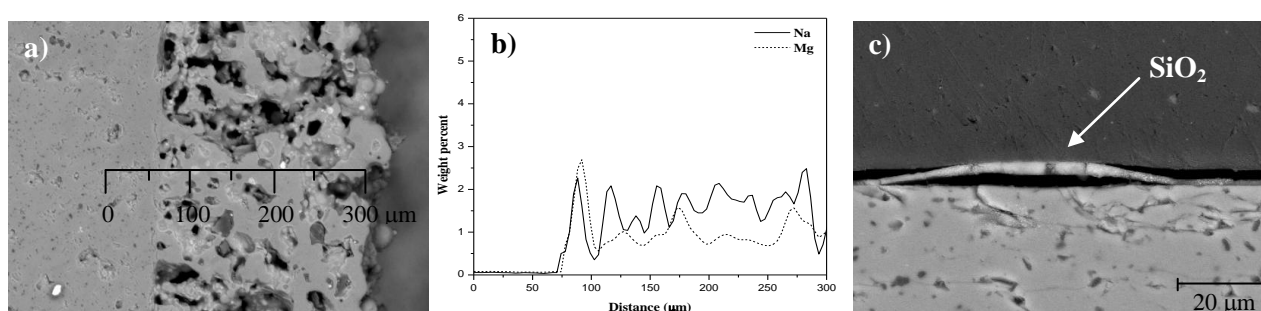


Fig. 7. Cross section morphology of coating exposed to corrosion test at 1000°C in Na_2SO_4 (a), concentration profile of Na and Mg in the cross section (b) and substrate exposed to oxidation test at 1300°C (c).

Summary

According to SEM observations, adherent, uniform and crack free fly ash cenospheres coatings were deposited on SiC substrates by electrophoretic deposition. Thermal treatments at 1200°C allowed the sintering of the coatings under a microwaves hybrid heating. The coatings exhibited high temperature oxidation and corrosion resistance and were highly successful in protecting the SiC substrates from aggressive environments.

Acknowledgment

The authors gratefully acknowledge Conacyt, Mexico for the provision of the research grant.

References

- [1] E.J. Opila and R. Hann, *J. Am. Ceram. Soc.* Vol. 80 (1997), p. 197-205.
- [2] S. Ueno, D.D. Jayaseelan, T. Ohji, and H.T. Lina, *J. Ceram. Process. Res.* Vol. 6 (2005), p. 81-84.
- [3] K.N. Lee, *J. Eng. Gas Turbines Power*, Vol. 122, 4 (2000), p. 632-636.
- [4] K.N. Lee, *Surface & Coatings Technology*, Vol. 133-134 (2000), p. 1-7.
- [5] D.C. Adriano, A.L. Page, A.A. Elsewi, A.C. Chang, I. Straughan, *J. Envir. Qual*, Vol. 9 (1980), p. 333-344
- [6] L.K.A. Sear in: *The properties and use of coal fly ash*, Chapter 1, The production and properties of fly ash, Thomas Telford Publishing, UK (2001).
- [7] G. Brunauer, F. Frey, H. Boysen, and H. Schneider, *J. Eur. Ceram. Soc.* Vol. 21 (2001), p. 2563-2567.
- [8] P. Sarkar, P.S. Nicholson, *J. Am. Ceram. Soc.* Vol. 79 (1996), p. 1987-2002.
- [9] T. Seike, M. Matsuda and M. Miyake, *J. Mater. Chem.* Vol. 12 (2002), p. 366-368.
- [10] D. Agrawal, J. Cheng, Y. Fang and R. Roy in: *Microwave processing of ceramics, composites and metallic materials*, edited by D.E. Clarke, D.C. Folz, C.E. Folgar and M.M. Mahmoud, *Microwave solutions for ceramic engineers*, The American Ceramic Society (2005) p. 205-228.
- [11] M. Gupta, W. Wai, L. Eugene, in: *Microwaves and metals*, Chapter 5 Microwave heating of other materials, John Wiley and Sons Pte. Ltd (2007).
- [12] A. Sussman, T.J. Ward, *RCA Rev.* Vol. 42(6) (1981), p. 178-97.
- [13] J.M. Andrews, J. Dracass, A.H. Collins, D.C. Cornish, *Proc. Brit. Ceram. Soc.* Vol. 12 (1969), p. 211-29.
- [14] C. Kawai, S. Wakamatsu, *J. Mater. Sci.* Vol. 31 (1996), p. 2165-70.
- [15] L.J. Vandeperre, O.O. Van der Biest in: *Innovative Processing and Synthesis of Ceramics, Glasses, and Composites*, *Ceram. Proc.* edited by N.P. Bansal, K.V. Logan, J.P. Singh, *Ceram. Trans.* volume 85, *Am. Ceram. Soc.* (1998).
- [16] N.S. Jacobson, *J. Am. Ceram. Soc.* Vol. 76(1) (1993), p 3-28.

Electrophoretic Deposition

doi:10.4028/3-908454-49-2

**Fly Ash Cenospheres Coatings by EPD-Microwave Sintering Process for SiC
Corrosion Resistance**

doi:10.4028/3-908454-49-2.201