FLY ASH/RARE EARTH OXIDES NANOCOMPOSITES FOR THERMAL BARRIER COATINGS PRODUCED BY ELECTROPHORETIC DEPOSITION

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Abstract. Fly ash is a ceramic waste material from coal fired power plants. A new alternative for its disposal is taking advantage of its good thermal properties and use it as the main raw material for the production of novel nanocomposites for thermal barrier coatings (TBCs) applications. The aim of this research was to produce a fly ash matrix TBC with low thermal conductivity and high thermal stability at high temperatures. Two rare earth oxides nanoparticles were chosen due to their low thermal conductivity, as reinforcements of a ceramic matrix nanocomposite. Electrophoretic deposition (EPD) technique was used for the preparation of these coatings due to its flexibility of use in different types of substrates and easy control of deposition thickness [1-3]. Different TBCs were obtained varying parameters such as time and DC voltage. Subsequently the coatings were submitted to different heat treatments in order to determine the most suitable sintering temperature. The sintered coatings were homogeneous and showed no crack formation. Morphological and microstructural characterization of TBCs produced with different EPD conditions and sintering temperatures have been performed. Additionally, thermal conductivity of the bulk samples was determined. These results confirm their potentiality as ultra-low thermal conductivity insulators for high temperature applications.

Introduction

Currently protective coatings like TBCs with a significantly lower thermal conductivity and higher thermal stability than existing coatings have a great application demand, like for example, to achieve ultra efficient systems [2] and increase service life time of engine and turbine components that work in high temperature atmospheres.The key to developing a TBC is selecting the raw material. Oxides with low thermal conductivity, high melting point, chemical stability with absence of phase transformations between room temperature and the work temperature of the component that is coated, are required to develop a TBC. Fly ash is a waste material from coal-fired power plants, which is building up day by day and its disposal becomes a serious problem of environmental pollution. It is for this reason that it is necessary to find new ways in which we can use this waste.

This waste is chemically constituted by mullite and a number of other oxides, it has a reported thermal conductivity of 0.47 W/mK at a temperature of 900 °C [11], also has a high melting point and is main characteristic is that has a morphology composed by hollow spheres, called cenospheres. There are many processes for the development of coatings such as APS or CVD, however, these processes are expensive, complex, involve many variables in the process and sometimes they are time consuming. That's why in this research we propose to work with the EPD process which is simple, cheap, fast and very flexible if you have complex morphologies substrates in addition to its facility to be scaled to an industrial level. The aim of this work is to found new stable phases with free SiO_2 present in fly ash, through additions of Gd_2O_3 and Nd_2O_3 nanoparticles in different concentrations, to produce improved TBCs by the EPD process.

Experimental procedure

Fly ash from Coahuila Mexico Electrical Power Plant was used as starting material. For the morphological characterization of fly ash and the coatings surface, scanning electron microscopy (SEM) analysis were carried out using a FEI Nova Nano SEM 200 system equipped with energy dispersive spectroscopy (EDS) and INCA software, resolution of 1.5 nm at 10 kV (under vacuum). Quantitative chemical composition of fly ash was determined using atomic absorption spectroscopy (AA) with a Thermo brand equipment and inductively coupled plasma (ICP) also with a Thermo brand equipment.The phases present in fly ash were identified using X-ray diffraction (XRD) (Empyrean, Panalytical diffractometer from Philips)), the counts were recorded from 5 to 100° (2θ) with a step of 0.017° (2θ), and a counting time of 40 s, using copper radiation. Fe_2O_3 was eliminated through a dry and wet magnetic separation process with neodymium magnets. In Addition, C was removed by calcination at 650 °C for 2 h. To determine the possible compounds of CCV with Gd_2O_3 and Nd_2O_3 with lower thermal conductivity, mixtures were made with different ratios of CCV and oxides. To each powder mixture were added 30 ml of acetone (JT Baker, with a purity of 99.6 %) and subsequently subjected to a conventional ultrasonic bath for 3 h, the mixtures were subjected to a heat treatment at 1000 °C with a heating rate of 10 °C/min for a period of 2 h. To determine if the formation of a new compound was successful, XRD was performed on each of the mixtures with the same equipment mention before. Thermal conductivity for different Fly ash-Gd_2O_3 and Fly ash-Nd_2O_3 composites was measured using a Heat Flow Meter Apparatus (ASTM C 518). Fly ash and fly as with addition of 10 and 20 wt% of Gd_2O_3 and Nd_2O_3 respectively were used to produce two identical coatings of each type with the same EPD conditions. 1 wt% of solids in acetone suspensions with addition of 2.5 mg of I_2 were prepared and put in an ultrasonic bath for a minimum of 2 hr The coatings were deposited on SiC substrates using 500 V for 3 min. One coating was sintered at 1100 °C and the other at 1200 °C, both for a period of 3 h with a heating rate of 5 °C/min.

The homogeneity of all the elements in the coating was determined by performing an X - ray elemental mapping of the surface of the coating with the EDS system mention before.

Results

XRD diffractograms and SEM micrographs of fly ash particles and the rare earth oxides used, Gd_2O_3 and Nd_2O_3 respectively are presented in Figure 1. Figure 1 (b) shows a broken sphere with different particles within, which shows that the morphology of fly ash is not only spherical but that is composed by hollow spheres (cenospheres). Furthermore you can see other particles with irregular morphology which are surrounded by smaller spheres. Similarly, in Figure 1 (d) we can see Gd_2O_3 nanoparticles which tend to agglomerate to form blocks, and in Figure 1 (f) we observed a micrograph of Nd_2O_3 nanoparticles which have a needle-type morphology and that tend to agglomerate randomly. Fly ash characterization by XRD is shown in Figure 1 (a), in which it can be seen that the ash sample has an amorphous portion, also has crystalline phases like SiO_2, an aluminosilicate compound ($Al_{4.52}O_{9.74}Si_{1.48}$) wish corresponds to mullite, and calcium carbonate ($CaCO_3$). With this equipment it was not possible to detect any other crystalline phase such as hematite (Fe_2O_3) because they are present in amounts below the detection limit of the technique.XRD diffractograms were also obtained for the selected oxides, for Gd_2O_3 are shown in Figure 1 (c) and for Nd_2O_3 is presented in Figure 1 (e). As can be seen Gd_2O_3 is crystalline and shows a single phase, while Nd_2O_3 shows otherwise. In Figure 1 (e) the upper diffractogram corresponds to commercial Nd_2O_3 without any treatment, however through XRD technique was identified that the powder did not correspond to Nd_2O_3 but to neodymium oxide carbonate ($Nd_2O_2CO_3$). Based on these results it was necessary to subject the material to a heat treatment of 1000 °C for 1 in order to remove the CO_2 content in the sample and obtain only Nd_2O_3. The lower diffractogram in Figure 1 (e) confirms that the thermal treatment worked and indeed the resulting material is now crystalline Nd_2O_3. Chemical analysis results of a fly ash sample are presented in Table 1, they show that fly ash consists mainly of SiO_2 and Al_2O_3 and other oxides compounds in small amounts, including Fe_2O_3, K_2O, MgO, TiO_2, Na_2O and CaO.

Table 1. Chemical composition of fly ash.

Powder	Mullite components (wt%)		Oxides content (wt%)						
	SiO_2	Al_2O_3	K_2O	MgO	TiO_2	CaO	Fe_2O_3	Na_2O	C
Fly ash	64.44	24.01	1.31	0.89	0.99	3.48	6.31	0.51	3.35
Fly ash after cleaning process	64.00	28.05	0.72	0.86	0.87	2.24	0.30	0.64	0.06

XRD diffractograms of powder samples of the different compounds of fly ash adding rare earth oxides are shown in Figures 2. In the diffractogram different phases such as mullite, SiO_2, as well as Gd_2O_3 and Nd_2O_3 were observed for each case, but new phases are also shown in both cases, corresponding to a gadolinium oxide silicate ($Gd_{9.33}(SiO_4)_6O_2$) and neodymium oxide silicate ($Nd_{9.33}(SiO_4)_6O_2$). Compounds with greater amount of silicate are formed containing 10 to 20 wt% of Gd_2O_3 and Nd_2O_3 respectively. Emphasizing in Figure 2 (a), we can see that compounds with greater presence of silicate are those containing 10 and 20 wt%. of Gd_2O_3. The highest peak of $Gd_{9.33}(SiO_4)_6O_2$ is in the compound containing 10 wt%. of Gd_2O_3. This same compound compared with others, has the smallest characteristic peak of Gd_2O_3, partly because it has less quantity but also for having reacted with SiO_2 more than the other compounds. Another noteworthy point is that the characteristic peak of SiO_2 is higher in the composite with 10 wt% of Gd_2O_3 that in the compound with 20 wt%, this may be due to the fact that the characteristic peak of the silicate and SiO_2 are too close, then the greater inflexion of the silicate could contribute to increased the peak height of SiO_2, and so the highest peak of the silicate would not be in the compound with 10 wt% of Gd_2O_3 but in the one with 20 wt%. This is why, to decide with which compound was the best , we took into account the results of the measurements of thermal conductivity and indeed the compound with lower thermal conductivity at room temperature was found to be the compound with 10 wt% of Gd_2O_3, later in this section the results obtained in these measurements will be presented. Figure 2 (b) shows the results of the XRD characterization of the compounds formed from the addition of Nd_2O_3 to a fly ash matrix. In the XRD diffractograms of the compounds corresponding to fly ash and Nd_2O_3, as in the compounds of fly ash and Gd_2O_3, compounds with 10 and 20 wt% of oxide are those with more presence of a silicate compound. In this case the greater presence of silicate are the compounds containing 20 wt%. of Nd_2O_3. As can be seen from the XRD all peaks corresponding to $Nd_{9.33}(SiO_4)_6O_2$ are higher than any of the other compounds, and the peaks corresponding to the SiO_2 are smaller in comparison with others. Therefore it was concluded that Nd_2O_3 reacted with the free SiO_2 present in fly ash. Just like with the Gd_2O_3 compounds thermal conductivity measurements at room temperature showed that this compound had the lowest value of thermal conductivity. It is for this reason that the ratio of fly ash-20 wt%. of Nd_2O_3 was chosen to continue experimenting and developing coatings. The results of the thermal conductivity measurements are shown in Figure 3 (a), as can be seen the compounds with lower thermal conductivity are: the compound of fly ash-10 wt%. of Gd_2O_3 and the compound of fly ash-20 wt% of Nd_2O_3, with 1.0274 and 1.9024 W/mK respectively. These data agree with the idea that the thermal conductivity decreases as the $Gd_{9.33}(SiO_4)_6O_2$ and $Nd_{9.33}(SiO_4)_6O_2$ is forming for each case.

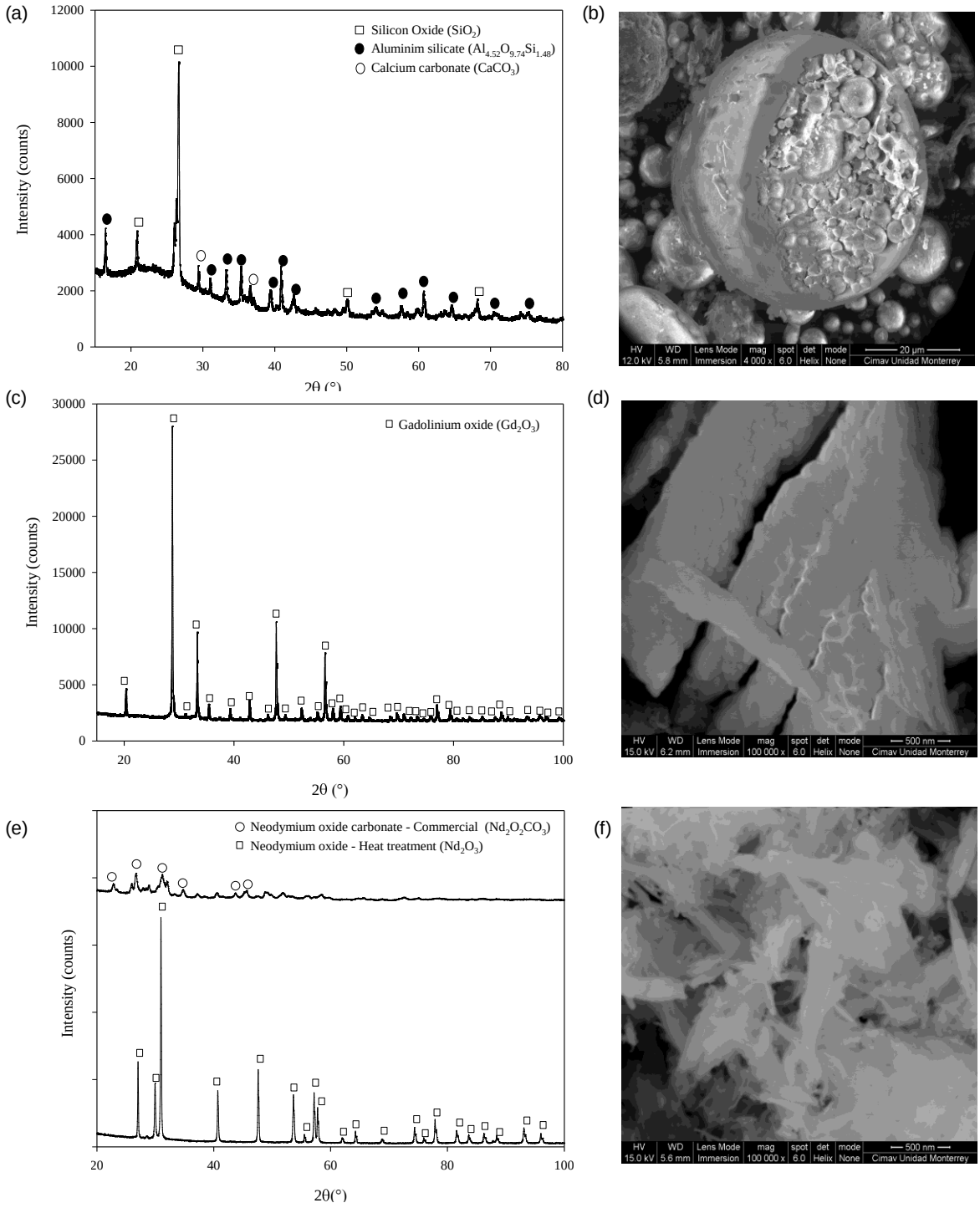


Figure 1. XRD diffractograms and SEM micrographs of (a) (b) fly ash, (c) (d) Gd_2O_3 nanoparticles and (e) (f) Nd_2O_3 nanoparticles.

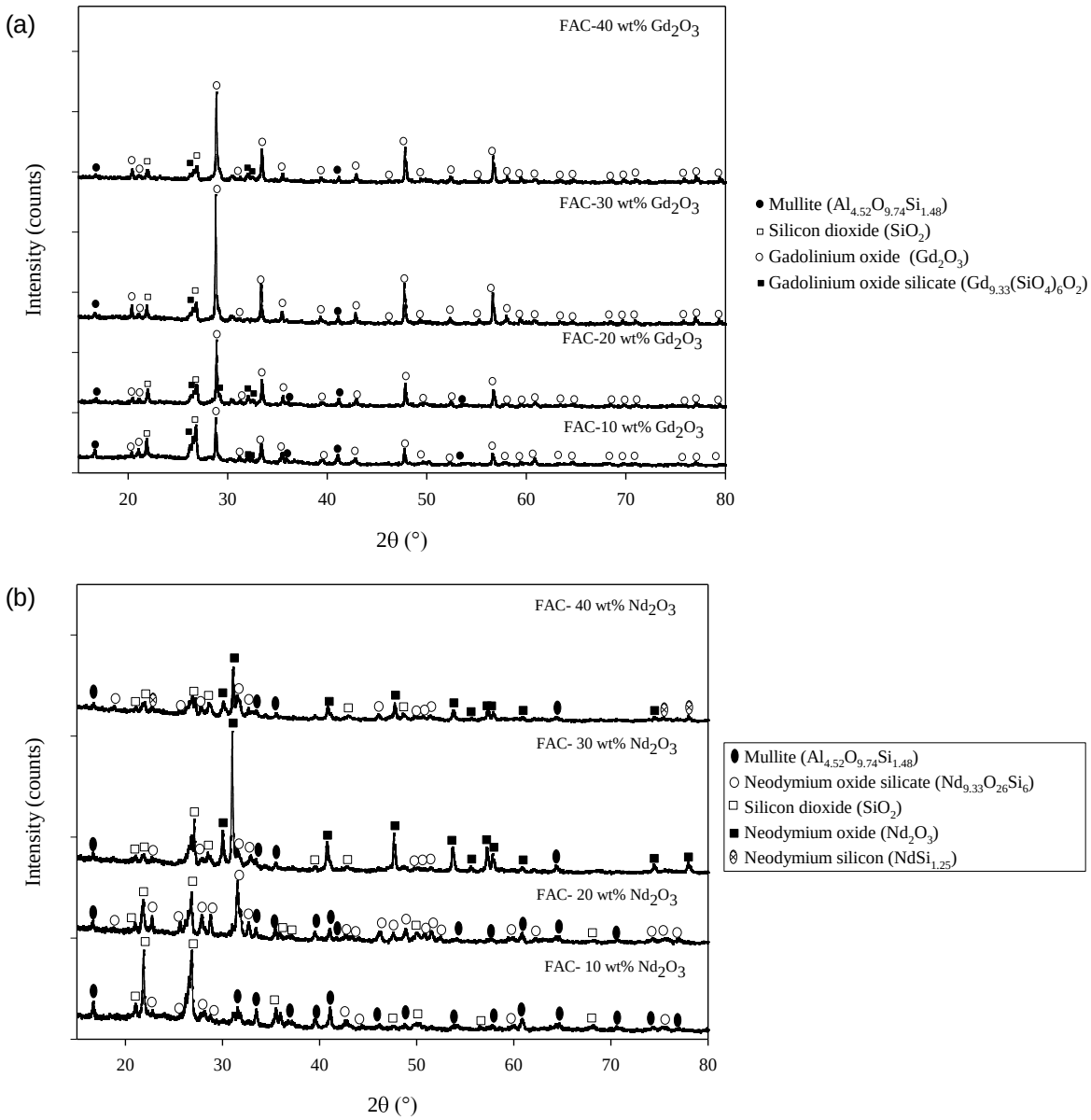


Figure 2XRD diffractograms of fly ash compounds with different amounts of (a) Gd_2O_3 and (b) Nd_2O_3.

Taking into account the two results the decision of discarding the rest of the compounds and only use the compounds of fly ash-10 wt% of Gd_2O_3 and fly ash-20 wt% of Nd_2O_3 to continue the development of TBCs was made. Figure 3 (b) shows plotted thermal conductivity values obtained for various materials developed for TBCs applications taken from the literature, that are being compared with the thermal conductivity values obtain for the new materials developed in this project. As shown in the graph all values of thermal conductivity of the materials developed in this research except the compound of fly ash-10 wt% of Nd_2O_3 have a lower thermal conductivity than the materials reported in the literature, being the compound of fly ash-10 wt% of Gd_2O_3, the one that has the lowest

conductivity of all. Tables 2 and 3 show a comparison of SEM micrographs taken at low (1000X) and high (10,000X) magnification respectively of fly ash, fly ash-10 wt% of Gd_2O_3 and CCV-20 wt% of Nd_2O_3 green and sintered at 1100 and 1200 °C coatings deposited on SiC substrates.

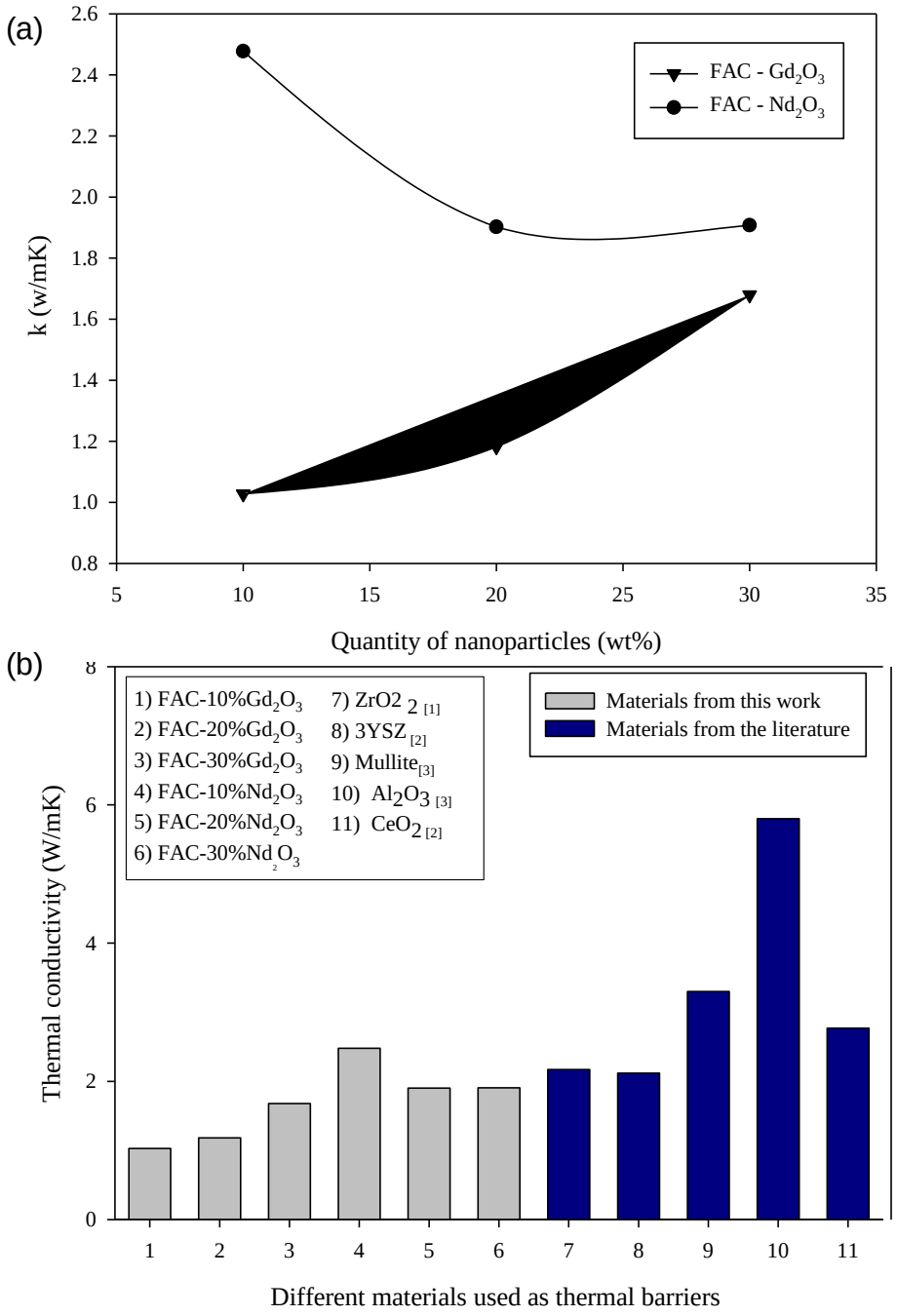


Figure 3. (a) Thermal conductivity values of fly ash compounds with different amounts of Gd_2O_3 y Nd_2O_3. (b) Comparison of thermal conductivity values of different materials used as TBC and the materials developed in this work.

Table 2. SEM micrographs taken at low magnification in green and sintered coatings on SiC substrates.

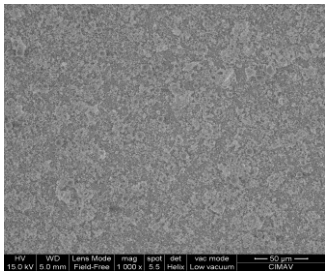
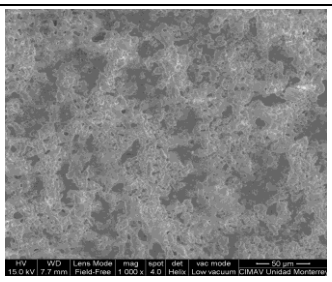
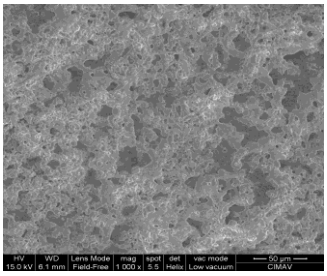
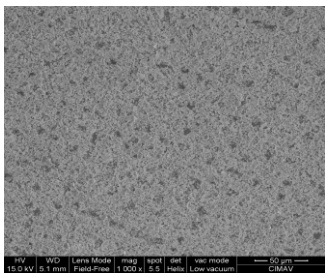
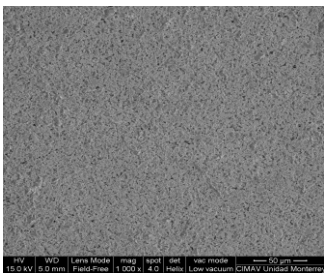
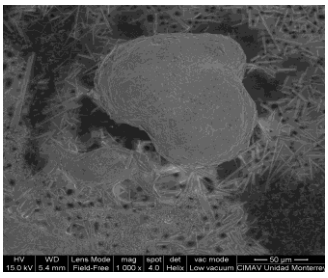
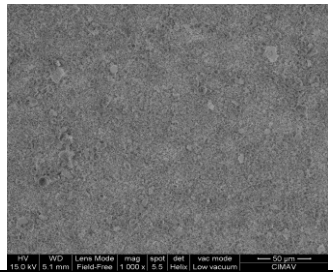
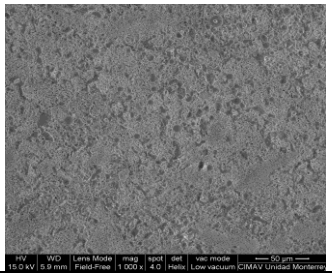
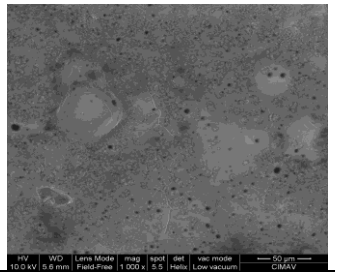
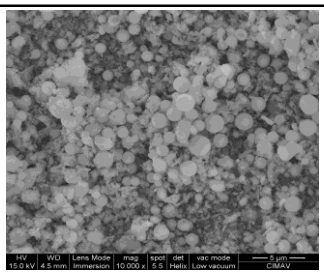
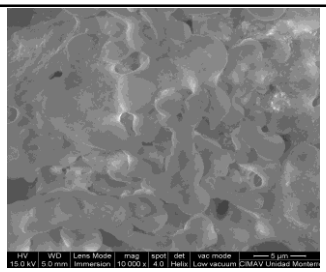
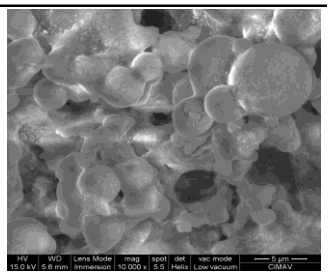
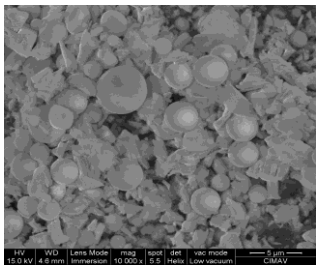
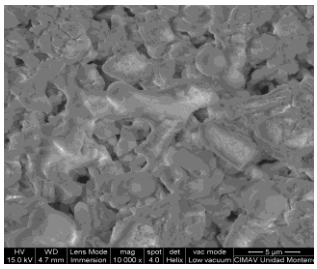
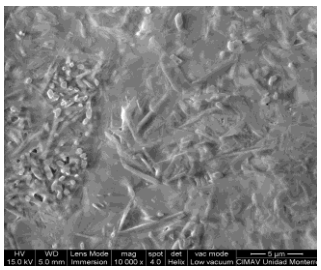
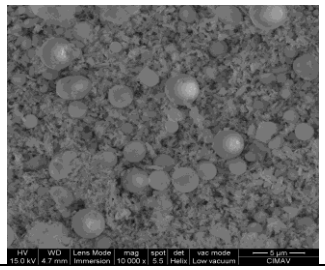
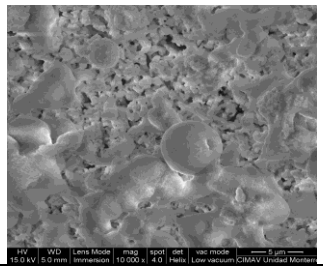
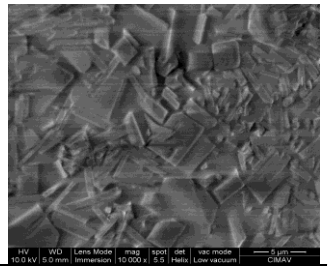
Material	Green coating	Sintered coating	
		1100 °C	1200 °C
Fly ash			
FA-10 wt% of Gd_2O_3			
FA-20 wt% of Nd_2O_3			

Table 3. SEM micrographs taken at high magnification in green and sintered coatings on SiC substrates.

Material	Green coating	Sintered coating	
		1100 °C	1200 °C
Fly ash			
FA-10 wt% of Gd_2O_3			
FA-20 wt% of Nd_2O_3			

Green coatings exhibit a homogeneous surface, however in this case the particles are physically attached only due to the arrangement that they were taking at the constant voltage application. Coatings sintered at 1100 °C are also uniform, have no cracks and they are porous. The coatings sintered at 1200 °C do not show all the same features fly ash coatings still show uniformity and porosity; however coatings of fly ash-10 wt% of Gd_2O_3 and fly ash-20 wt% of Nd_2O_3 are not uniform. In the fly ash-10 wt% of Gd_2O_3 coating some particles began to melt and form agglomerates and in the fly ash-20 wt% of Nd_2O_3 the porosity is lost and different cracks appear, these features are undesirable in a TBC. Figure 4 (a) and (b) shows X-ray elemental mapping of a coating of fly ash-10 wt% of Gd_2O_3 and a coating of fly ash-20 wt% of Nd_2O_3 respectively. In this case both coatings show the same pattern, where one can easily see that the Nd and Gd is uniformly distributed over the entire coating.

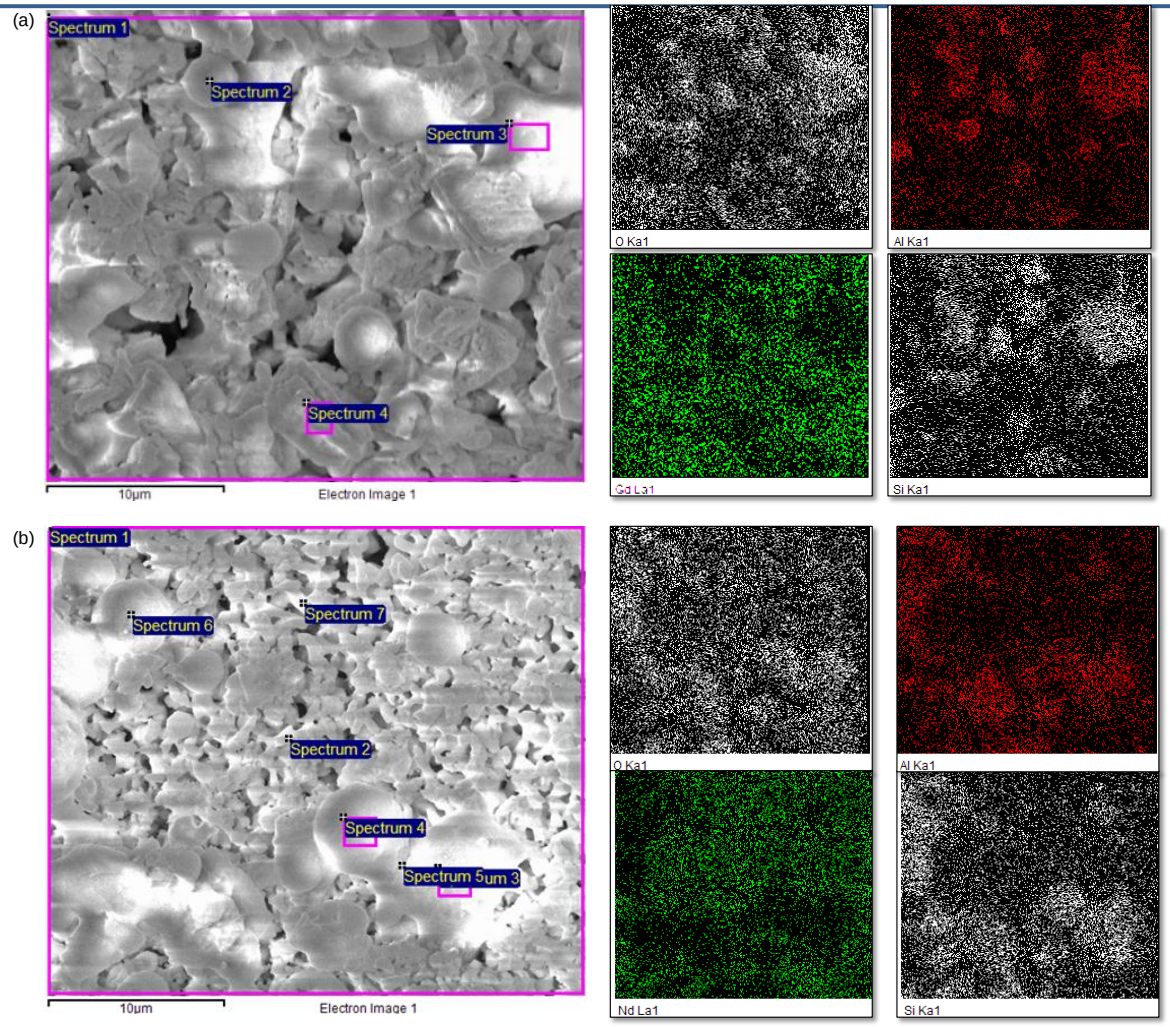


Figure 4. X-ray elemental mapping of coatings of (a) fly ash-10 wt% of Gd_2O_3 and fly ash-(b) 20 wt% of Nd_2O_3 both sintered at 1100 °C.

Summary

The thermal conductivity measurements of different mixtures of fly ash and rare earth oxides showed that FA-10 wt% of Gd_2O_3 and FAC-20 wt% of Nd_2O_3 nanocomposites have lower conductivity than other materials used as TBCs reported on the literature. Homogeneous and compact coatings of Fly ash/rare earth oxide were successfully deposited by EPD without cracks at 500 V during 3 minutes reaching. Formation of neodymium oxide silicate ($Nd_{9.33}O_{26}Si_6$) and gadolinium oxide silicate ($Gd_{9.33}(SiO_4)_6O_2$) compounds were both formed with thermal treatment at 1100°C during 3 hours. The thermal behaviour and stability of nancomposites at high temperatures is currently underway.

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