Fly ash/rare earth oxide coatings by EPD: Processing and characterization

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Abstract. Novel materials that can be used as thermal barrier coatings in high temperature applications were obtained by homogenization, mechanical milling and thermal treatment. Samarium oxide was investigated as an alternative to react with the free silica from fly ash and to form new silicate compounds. The main phases found in fly ash-Sm_2O_3 mixtures were mullite and samarium silicate $Sm_{4.66}O(SiO_4)_3$. Electrophoretically deposited coatings from these materials were obtained at 50 V and 3 minutes deposition time. The surface microstructure of the coatings was characterized by scanning electron microscopy (SEM-EDXS). The coatings were homogeneous and showed no crack formation. Additionally, thermal conductivity of the bulk samples at room temperature was determined. The thermal conductivity values of the new materials were below 1 W/mK which makes them suitable for thermal and environmental barrier applications.

Introduction

Ceramic thermal barrier coatings (TBCs) are receiving increased attention for advanced gas turbine engine applications. TBCs are considered technologically important because of their ability to further increase engine operating temperatures, and to achieve engine efficiency, emission and performance goals. Advanced thermal barrier coatings that have significantly lower thermal conductivity and better thermal stability than current coatings must be developed for future ultra efficient, low emission engine systems. Thermal and environmental barrier coatings can give protection from high temperature environmental attack; extend the durability and mechanical properties of components, increase operation temperature and reduce cooling requirements [1,2]. The most common thermal barrier coating is Yttria-Stabilized Zirconia (YSZ) because it has high thermal expansion coefficient, low thermal conductivity and high thermal shock resistance, however the main disadvantage in this material is its phase transformation and oxidation at working temperatures [3]. Other materials that can be used are mullite and lanthanum zirconium oxide ($La_2Zr_2O_7$). For example, mullite has low thermal conductivity, good thermal shock resistance, high corrosion resistance and low thermal expansion coefficient. In addition, $La_2Zr_2O_7$ presents high thermal stability, low thermal conductivity and low thermal expansion coefficient [3]. An important source of mullite is fly ash (FA). Fly ash is a waste material from coal combustion plants in electricity generation, and is composed mainly of silica and alumina in about 80 wt%, and also has a high quantity of amorphous material [4]. The motivation to use it in this research is because globally, coal-fired power plants produce approximately 500 million tons of fly ash each year [5]. In Mexico, two power generation plants located in north Coahuila produce about 1.62 million tons annually [6].

The aim of this work is to study new phases formed between free SiO_2 from fly ash and samarium oxide through mechanical milling and thermal treatment. The new FA-Sm_2O_3 powders are

electrophoretically deposited for applications as TBCs stable at high temperatures. The first results of thermal conductivity of these materials are tested by the Guarded Hot Plate technique [7].

Experimental procedure

Fly ash from Coahuila Mexico Electrical Power Plant was used as starting material. Fe_2O_3 was eliminated through dry magnetic separation process via an L-1 magnetic roller separator (S.G. Frantz Company). In addition, C was removed by calcination at 700°C for 2 h. Commercial Sm_2O_3 (Metall Rare Earth Limited, China) was subjected to a heat treatment at 600°C during one hour to eliminate moisture. After these pretreatments, FA powder and Sm_2O_3 in different concentrations were milled during 60 hours at a speed of 400 rpm using zirconia balls in an atrittion mill system to obtain stable compounds with the free silica from fly ash. Crystallographic evolution of the FA-Sm_2O_3 mixtures was determined by X-ray diffractometry (XRD) (PANalytical Empyrean Diffractometer from Philips) with Cu Kα radiation (1.54 Å under conventional diffraction geometry (2θ scanning) with generator settings of 40 mA and 45 kV. Differential thermal analysis was performed to powder samples in a TA Instruments SDT Q600 equipment, using alumina crucibles at a heating rate of 10°C/min from room temperature to 1300°C with a flow of 100 ml/min nitrogen gas. The thermal conductivity of FA-Sm_2O_3 uniaxial pressed powder compacts was measured at room temperature with the Guarded Hot Plate technique according to ASTM C177 Standard [7]. Next, suspensions of FA-Sm_2O_3 powders were made in acetone using 1 wt% solids content. Subsequently, the suspensions were dispersed in an ultrasonic bath (Fisher Scientific Model 500) during 30 min and then sedimented for 5 min. This procedure allowed the elimination of the largest particles. The zeta potential of the obtained samples was measured in a Zetatrac Equipment Model NPA152−31A with an internal sample cell volume of 0.7−3 ml. The method to approximate the pH in acetone was through modifications to the suspension with additions of hydrocloric acid (HCl) aqueous solution (0.01M) and sodium hydroxide (NaOH) aqueous solution (0.1M) to check the stability at different pH values using a micro dropper. FA-Sm_2O_3 coatings were then deposited by EPD on 316 L stainless steel substrates. A voltage of 50 V was applied to the suspensions during 1, 3 and 6 minutes. Finally surface morphology and composition of the coatings was analyzed by SEM-EDXS. 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).

Results

Fig. 1 shows the XRD patterns of starting materials and mixtures of fly ash with Sm_2O_3 in two different concentrations. As it can be seen, the main phases in fly ash after thermal treatment at 700°C during 2 hours to eliminate the C content are mullite, quartz and also an amorphous phase. From the crystalline part of fly ash, the percentage of phases is 57% mullite and 43% quartz (wt% according to relations of relative intensity in X-ray diffraction pattern). Also, Fig. 1 shows the XRD pattern of commercial Sm_2O_3 after heat treatment at 600°C showing the pure oxide. Fly ash with addition of 10 wt% Sm_2O_3 after 60 hours milling, presents the phases quartz, mullite, Sm_2O_3 and in minimal quantity Fe_2O_3 and no formation of new compounds. Increasing the content of Sm_2O_3 from 10 to 30 wt% without milling and, with homogeneization and heat tretament at 1000°C during 2 hours, shows that the main phases found in both mixtures are mullite, a new compound known as samarium silicate with stoichiometric formula $Sm_{4.66}O(SiO_4)_3$ and a low quantity of SiO_2. As it can be seen, increasing the quantity of Sm_2O_3 increases the formation of samarium silicate and decreases the amount of free silica in the material. The absence of the samarium silicate in the pre-milled powder was because ball milling technique mechanically heats and releases energy but not enough for a reaction of SiO_2 and Sm_2O_3. On the other hand, the amorphous phase present in fly ash as starting material is more reactive to form new phases with the Sm_2O_3 when increasing

temperature as it can be seen by the formation of the new samarium silicate for samples with thermal treatment at 1000°C.

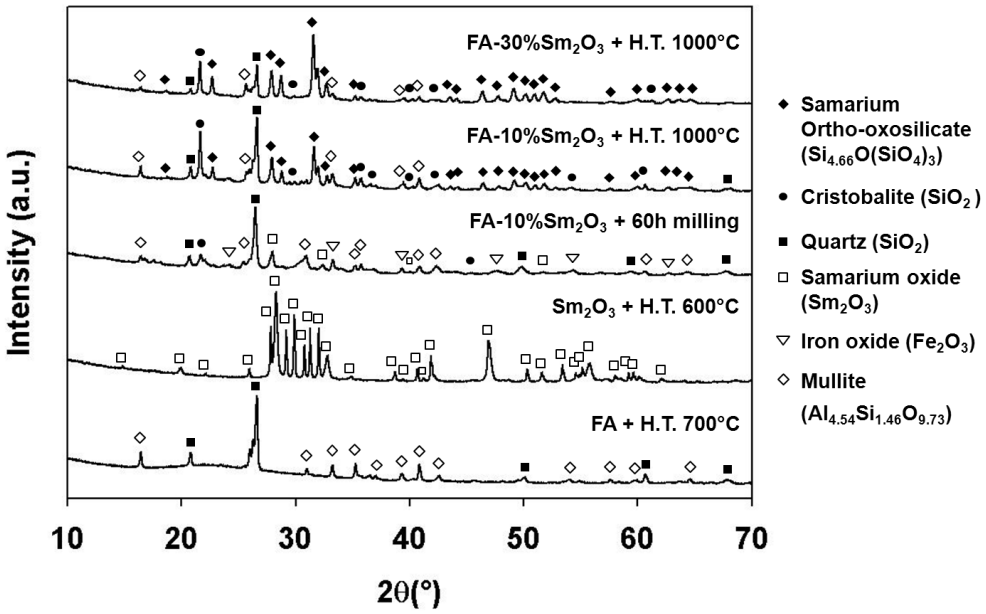

Fig. 1. XRD patterns of starting materials and mixtures of fly ash and Sm_2O_3 in two different concentrations.

Fig. 2 shows the differential thermal analysis of fly ash and mixtures of FA-Sm_2O_3 after thermal treatment. As it can be seen in the thermogram obtained from the starting fly ash, at 650°C there is an exothermic peak corresponding to the elimination of carbon in the sample. Around 900°C there is a small peak that corresponds to silica phase transformations and at 1250°C the beginning of sintering of the material and crystallization of mullite takes place. As shown in the graph, the materials that contain a high quantity of the new compound samarium silicate are stable from room temperature up to approximately 1200°C, where possibly begins some transformation of the remaining free silica in the material. The exact quantity of Sm_2O_3 that is required to eliminate the free SiO_2 in fly ash has to be optimized. Samarium silicate can be stable up to 1180°C without any phase transformation indicating that it can be a potential material for thermal and environmental barrier coatings.

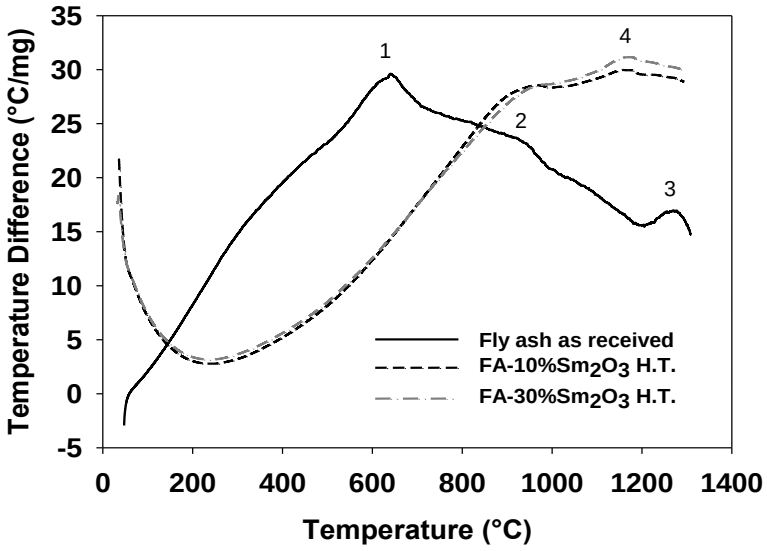

Fig. 2. Differential thermal analysis curves of fly ash as received and mixed with Sm_2O_3 in different concentrations.

The thermal conductivity measurements of FA-Sm_2O_3 mixtures are presented in Fig. 3. All the values of these new materials are below 1 W/mK which makes them attractive for thermal barrier applications. From this graph it can be seen that the material with the lowest thermal conductivity is FA-10%Sm_2O_3 (wt%) mixture thermally treated al 1000°C during 2 hours, showing a value of 0.38 W/mK. In comparison with other materials used as thermal barrier coatings, the materials proposed in this work have lower values of thermal conductivity in bulk than for example, mullite or CeO_2 [9,10]. It is important to mention that these values were measured at room temperature and measurements of this property at high temperatures are required to evaluate the stability of the new compound found. Also, the measurements of conductivity in the coatings are expected to be even lower due to porosity and microcracks usually found.

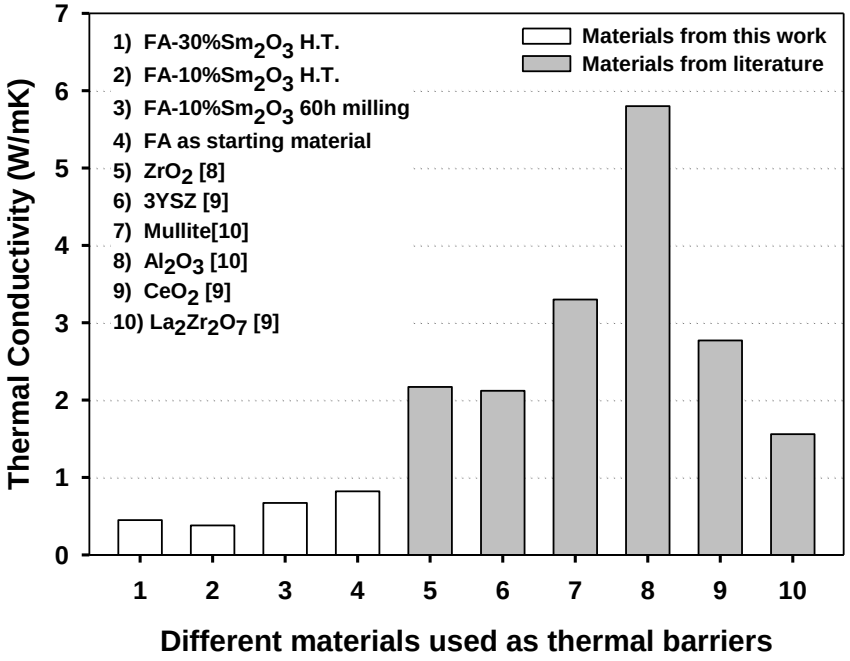

Fig. 3. Thermal conductivity at room temperature of different materials used as thermal barriers.

On the other hand, Fig. 4 presents the results of zeta potential measurement of FA-30%Sm_2O_3 mixture (wt%) in an acetone suspension which was selected because has a better stability according to a previous work focused on EPD of fly ash [11]. Without additions of HCl and NaOH, the suspension had high stability with a zeta potential of -75 mV, therefore this condition was used to carry out the EPD experiments. The suspension behaviour is positive zeta potential at low pH and negative zeta potencial at high pH with an isoelectric point about 5.5.

Finally Fig. 5 shows SEM surface morphologies and composition of FA and FA-Sm_2O_3 obtained at 50 V during 3 minutes by EPD: fly ash coating (5a and 5b), FA-10%Sm_2O_3 coating (wt%) (5c and 5d) and FA-30%Sm_2O_3 coating (wt%) (5e and 5f). It is clear that the microstructure of the samples is formed by irregular particles with a homogeneous coating that completely covers the substrate (Fig. 5a). As it can be observed, fly ash coating has high concentration of mullite and silica and some others oxides such as CaO, Fe_2O_3 and TiO_2 which are in low quantities (Fig. 5b). The surface microstructure of the coatings containing the new compound samarium silicate are homogeneous and do not present cracks (Fig. 5c (10 wt%) and 5e (30 wt%)). Samarium silicate is observed as bright small irregular particles distributed within the mullite matrix and with heat treatment some particles begin to agglomerate. It is important to mention that coatings obtained with longer deposition times of 6 minutes showed no cracking. However, for coatings prepared from fly ash with addition of 10% Sm_2O_3 with 60 h milling, higher deposition times meant more thickness and cracks during drying. From the chemical point of view, these coatings have a higher quantity of free

silica and from the physical point of view, there are stresses due to very small particles sizes and strong capillary forces during drying.

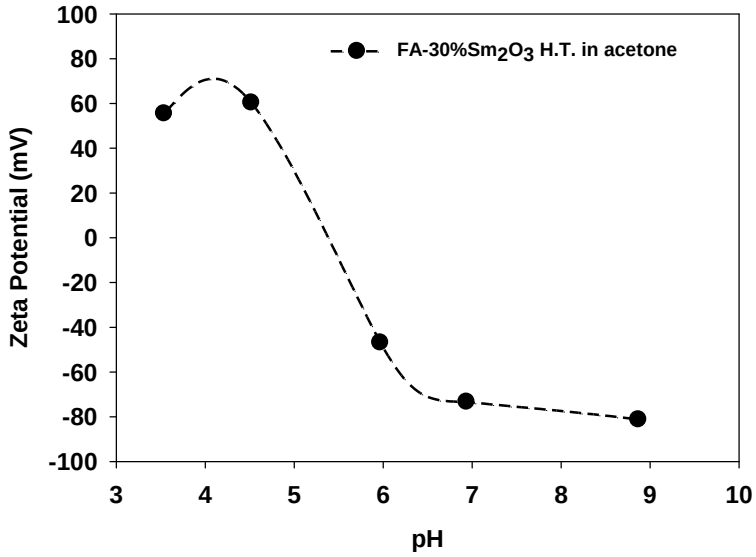

Fig. 4. Zeta potential measurement of fly ash-30%Sm_2O_3 (wt%) thermally treated.

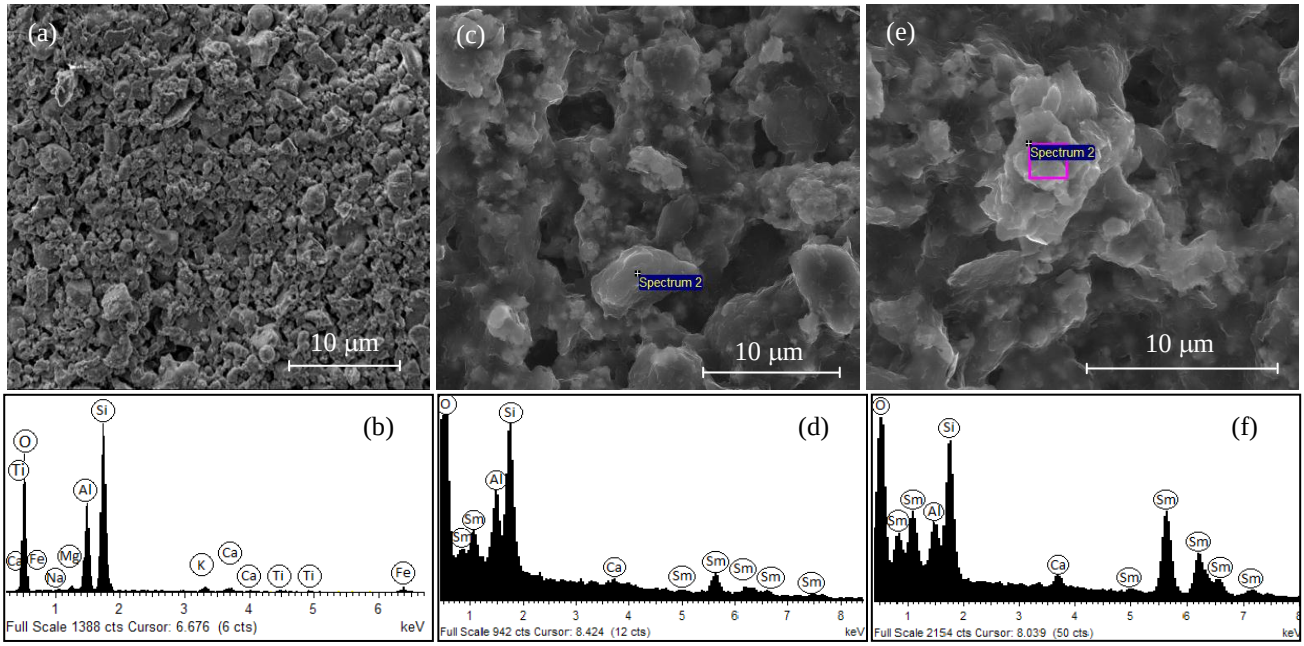

Fig. 5. SEM-EDXS of fly ash coating microstructures (a and b) and mixtures of FA-Sm_2O_3 showing the morphology and composition of samarium silicate particles (c to f).

Summary

Fly ash/rare earth oxide coatings were successfully deposited by EPD at 50 V during 3 minutes. Formation of samarium silicate (Ortho-oxosilicate $Sm_{4.66}O(SiO_4)_3$) compound is possible with thermal treatment and short or no milling time. The optimal quantity of Sm_2O_3 added to fly ash, in order to form a new compound, has to be optimized. In samples with no heat treatment, increasing deposition time (6 minutes) increases the amount of cracks in the coating. The formation of new compounds by heat treatment opens the possibility to use only the spherical/hollow material in FA for the preparation of coatings with higher porosity. The thermal conductivity values of the new bulk materials obtained in this work are well below 1 W/mK which makes them suitable for thermal barrier applications.

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