Passivation of Al_2O_3-based Refractories by Air Plasma Spray Coatings of Y_2O_3

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1. Introduction

As the starting process of pyroprocessing, head-end process deals with the conversion of spent fuel into suitable feed form of uranium oxides for following electrolytic reduction process. Depending on its physical form, the fabrication process of feed materials may (or may not) include high temperature treatment. Voloxidation and sintering correspond to the high temperature processes in the preparation of porous pellet, which is one of the promising feed materials [1-3]. During the heat treatment at high enough, radioactive fission products such as Cesium (Cs) and Iodine (I) are released from the spent fuel of uranium oxides. Considering that the fission products are extremely harmful to human body, their emission to atmosphere must be strictly minimized by capturing them using appropriate filters. In other words, the released off gas should be collected at the filters connected to a furnace where the heat treatment of the spent fuel takes place.

The off-gas escapes from the spent fuel and move to the filters along with atmospheric gas flow in heating furnace, contacting inner surfaces of the refractory materials in the furnace. Most of the refractories usually contain alumina (Al_2O_3) and silica (SiO_2) due to their excellent heat tolerance. However, those likely to form mullite ($Al_6Si_2O_{13}$) phase during heating. The mullite is well known material for capturing the Cs vapor by the formation of pollucite ($CsAlSi_2O_6$) phase. Considering this, the use of those general refractories would be a critical problem. Apart from developing 'brand-new' refractory materials, which is extremely challenging, the coatings of inert materials on the surface of refractories can be a possible detour to suppress the reaction with CS. The present study explores the possible way to prevent the capture reaction of Cs with refractories by Air Plasma Spray (APS) coating of pure Y_2O_3. Both confirmation on the material and optimization of the coating process in this study would provide the applicability of this material and method for successful head-end process, especially for capturing the off-gas in pyroprocessing.

2. Experimental

The commercial insulating fire bricks with a composition of 99.3Al_2O_3-0.4SiO_2-0.1Fe_2O_3 (wt. %) and high purity Y_2O_3 powder (> 99.9 %) were prepared for the substrate and coating material for APS coating in this experiment. The confirmation on the reactivity of the Y_2O_3 with Cs using Cs_2CO_3 powder, which is decomposes into Cs_2O and CO_2 after melting at about 610°C. The spray coating was conducted with the same conditions except the thickness of Y_2O_3 coating layer then optimized the thickness of coating layer as 500 μm. To enhance adhesion without delamination, the coated samples were heat-treated at 1520°C for 10 h in air atmosphere with heating and cooling rate of 2°C/min. For the reaction experiment between Cs and refractory material, Cs_2CO_3 powder was used as Cs source. 0.05 g of Cs_2CO_3 powder was dispersed on the surface of coated layer and heat treated at 1450°C for 1 h in 4% H_2-Ar flow (0.1 liter/min). The characterization was conducted by SEM/EDS and XRD before and after the heat treatment.

3. Results and Discussion

Fig. 1 shows the physical properties of the commercial insulating brick. It consists of pure Al_2O_3 particles ranging from few to few tens of microns as shown in the SEM and SEM/EDS results. Their particle shapes varied from rounded to elongated. The XRD pattern indicates its single phase of Al_2O_3. To exclude the possibility of mullite phase is the reason why the brick of high purity without Si was used in this experiment.

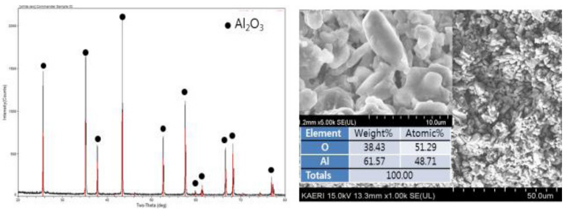

Fig. 1. XRD (left) and SEM/EDS results of the brick.

Fig. 2 shows SEM micrographs of the cross section and the surface of Y_2O_3 coated samples after heat treatment at 1520°C for 10 h in air. Clear distinction was made by different porosity in the observations. It is noting that the substrate brick was overspread with coated Y_2O_3 layer. From the micrograph showing the surface of the coated layer, well-organized small Y_2O_3 grains were observed. Severe roughness with many pores was also observed at the surface which is largely due to the original surface roughness of the surface of brick substrate. However, it did not mean the exposure of the substrate brick to atmosphere.

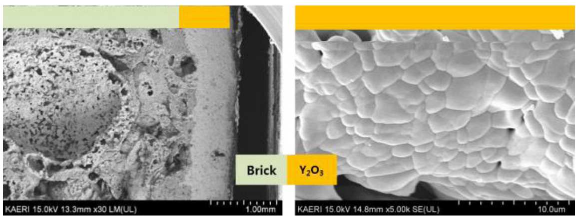

Fig. 2. SEM micrographs showing a cross section (left) and surface (right) of the APS coated samples.

The spatial chemical composition across the interface was observed by SEM/EDS line scan as shown in Fig. 3. It shows other distinction of the substrate and coated layer than the morphology shown in Fig. 2. The brick substrate and coated layer were divided by its composition with other major cation element, Al and Y, respectively. In the line scan result, some of Al was also observed at the coated Y_2O_3 layer. In contrast, from the spot analysis indicated that the coated layer was homogeneous Y_2O_3 single phase, indicating the inactivation of the coated layer based on that there was no reaction between the Y_2O_3 and Cs_2CO_3 powder.

Fig. 4 shows the photographs of cube-shaped samples before and after heat treatment at 1450°C for 1 h in 4% H_2-Ar, which is similar with real sintering process of the porous pellet fabrication.

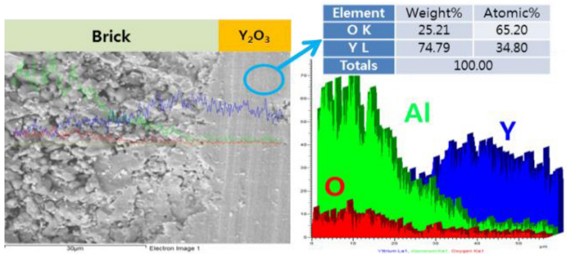

Fig. 3. SEM/EDS line scan result of across the interface between brick and coated Y_2O_3 layer.

The heat treatment was accompanied by addition of Cs_2CO_3 powder on the surface of the coated Y_2O_3 layer. After the heat treatment, the coated layer was Y_2O_3 single phase as shown in the XRD pattern as it was before the heat treatment. This clearly indicates that there would be no chemical reaction of the coated Y_2O_3 layer with Cs.

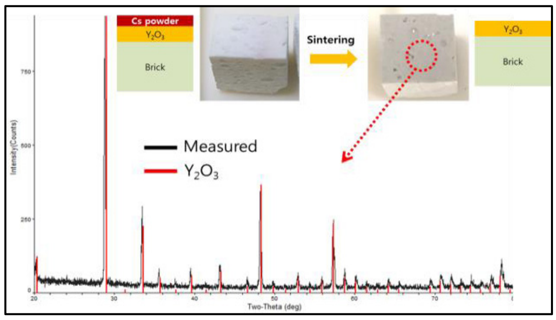

Fig. 4. Photographs of the samples before and after heat treatment (inset) and XRD pattern of the coated Y_2O_3 layer after heat treatment.

4. Conclusions

The coated Y_2O_3 layer on a commercial fire brick maintained its physical/chemical integrity with the presence of Cs during high temperature heat treatment. This provides the applicability of the APS coating of Y_2O_3 to the refractories for off-gas treatment system in pyroprocessing.

REFERENCES

[1] Y. Sakamura and T. Omori, "Electrolytic Reduction and Electrorefining of Uranium to Develop Pyrochemical Reprocessing of Oxide Fuels," Nucl. Techno., 171 (2010) 266–275.

[2] S.-C. Jeon, J.-W. Lee, J.-H. Lee, S.-J. Kang, K.-Y. Lee, Y.-Z. Cho, D.-H. Ahn, and K.-C. Song, "Fabrication of UO_2 Porous Pellets on a Scale of 30 kg-U/Batch at the PRIDE Facility," Adv. Mater. Sci. Eng., 2015 (2015) 1-8.