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CVR-SiC coating of graphite pebbles for fusion blanket application

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Abstract

The Helium Cooled Ceramic Reflector (HCCR) Test Blanket Module (TBM), recently planned for installation and testing in the nuclear fusion energy project of International Thermonuclear Experimental Reactor (ITER), uses graphite in the form of pebbles as a neutron reflector, opening the possibility of avoiding the use of a beryllium neutron multiplier. A silicon carbide (SiC) coating should be formed on the graphite pebbles to prohibit the reaction of graphite with steam and/or air and to reinforce the surface strength. In this work, a dense β-SiC coating was formed over the surface of the graphite pebbles by a chemical vapor reaction (CVR) process of the solid–solid (SS) and vapor–solid (VS) reaction of the $SiO_2(s)$–C(s)–SiO(v)–CO(v) system. The microstructural features, XRD patterns, pore size distribution, porosity and oxidation behavior of the SiC-coated graphite pebbles were investigated. A SiC coating with a thickness of approximately 30 μm remarkably improved the oxidation resistance and the density of the graphite pebbles. In an isothermal oxidation test conducted at 700 °C, the SiC-coated graphite pebbles showed strong oxidation resistance and a weight loss of approximately 2 wt% over the course of 2 h. This paper describes the major results obtained from our experiments on the CVR-SiC coating of nuclear graphite pebbles, recently conducted in the Korean HCCR TBM team of the ITER project.

Keywords: International Thermonuclear Experimental Reactor (ITER); Korean Helium Cooled Ceramic Reflector (HCCR) Test Blanket Module (TBM); Neutron reflector graphite pebbles; Chemical Vapor Reaction (CVR)-SiC(Silicon Carbide) coating

1. Introduction

The Korean Helium Cooled Ceramic Reflector (HCCR) Test Blanket Module (TBM) was designed to test the performance of DEMO-relevant blankets. A lithium ceramic breeder material, beryllium neutron multiplier, and graphite neutron reflector are used in pebble-bed forms. One of the unique features of the HCCR TBM is that a reflector is used to reduce the amount of beryllium [1]. Graphite has been considered as a reflector material for neutron irradiation. During the operation of a fusion reactor, graphite pebbles must endure the harsh environment of neutron irradiation [2]. Graphite is used in a pebble-bed form to accommodate any possible geometrical changes due to neutron irradiation. In addition, a thick graphite reflector can act as a heat sink in the case of loss of coolant accidents.

The CVR-SiC coated graphite pebbles are considered to prohibit the reaction of graphite with steam or air and to reinforce the surface strength at elevated temperature. Protective SiC coatings have been widely used in the steel and microelectronic industries because of their intrinsic properties, such as good wear resistance, high hardness, high thermal conductivity and very high thermal stability [3]. Our previous studies have been mainly focused on the formation of SiC coatings on graphite substrates by wet coating technology or by RF sputtering using a sintered SiC target [4,5].

Although, chemical vapor deposition (CVD) has been widely utilized to form coatings, SiC coating layers for components with complex shapes such as spherical pebbles can be more easily formed by the CVR method than by the CVD method [6,7]. In addition, the SiC conversion layer formed via the CVR method adheres well to graphite matrices. The CVR process is based on carbothermal reduction, in which silica reduction is carried out with a carbon source. The CVR process is independent of the molar ratio of silica to carbon; ultimately, silica reduction with a SiC source is excluded from the overall process ($SiO_2+3C \rightarrow SiC+2CO$). Of particular importance to SiC phase nucleation is the generation of SiO from the silica–carbon reaction [8]. With the formation of SiO and CO vapor ($SiO_2+C \rightarrow SiO+CO$), the surfaces of graphite pebbles are coated

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with polycrystalline SiC through a reduction reaction between SiO and a carbon source ($SiO+2C \rightarrow SiC+CO$) [9–11].

In this study, SiC coatings were formed on graphite pebbles by the CVR process for HCCR TBM neutron reflector applications. This work describes the results of our preliminary experiments regarding the SiC coating layers of graphite pebbles fabricated by the CVR process.

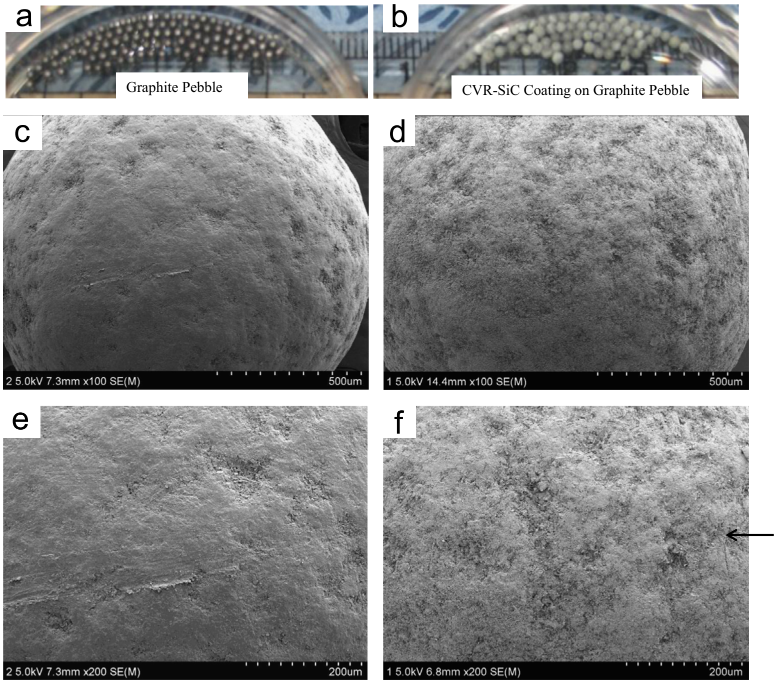
2. Experimental

In this work, silica (SiO_2) powder (average particle size: 3 μm, NOA Technology, USA) and finely ground spherical graphite pebbles measuring approximately 1 mm in diameter were used to form a SiC conversion layer. Additional carbon material was used as an excess carbon source for silica reduction. Silica powder and graphite pebbles (IG-11, density: 1.77 g/cm^3, Toyo tanso Co.) were placed in a graphite crucible and then heated to over 1700 °C with nitrogen gas flow. To control both the reaction conditions and the SiO and CO partial pressures during the CVR process, the graphite architecture designed was used. To compare the CVR coating layers according to shape and surface condition, the surfaces of graphite cubes measuring $8 \times 8 \times 8$ mm^3 and $2 \times 2 \times 2$ mm^3 were ground using SiC abrasive paper #800, 1000, 1500, and 2000; then, the ground graphite specimens were placed in a graphite crucible filled with SiO_2 powder. The same amount of SiO_2 powder was used for each specimen because the discharge behavior of SiO and that of CO during the CVR process must be made to be as similar as possible. The inside of the graphite crucible was coated with spray-coated BN and covered with graphite foil to prevent reaction with the silica melt.

The oxidation behavior of the CVR-SiC coating layer formed over the graphite pebbles was investigated by DSC/TGA (differential scanning calorimetry/thermogravimetric analysis, differential scanning calorimeter (DSC SDT Q600, TA instruments). The SiC-coated graphite pebbles in the DSC/TGA instrument were heated to 700 °C under flowing Ar gas; the pebbles were held at this temperature for 3 h, blowing air at a rate of 100 ml/min. The SiC conversion layer was analyzed using an X-ray diffractometer (X-Pert Pro, PHILLIPS). A half section of these spherical specimens was removed by grinding with abrasive pad, and then, other half section of these specimens was polished with abrasive slurry. The cross-section of the SiC conversion layer was observed by FE-SEM (HITACHI S-4800, Japan) and EDS analysis. The pore size distribution of the CVR-SiC coating was analyzed by mercury intrusion porosimetry (AutoPore IV 9500 MICROMERITICS INSTRUMENT).

3. Results and discussion

The SiC coating layers have been successfully prepared on graphite pebbles by the CVR process at temperatures ranging from 1750 °C (2 h) to 1850 °C (2 h). Fig. 1 shows images, the surface morphologies and the atomic ratio obtained by EDS analysis of the CVR-SiC-coated graphite pebbles obtained at 1750 °C (2 h) and the ground bare graphite pebbles. After formation of the CVR-SiC coating, the prepared specimen exhibited a slight change in surface morphology. EDS elemental



Element	Weight%	Atomic%
C K	29.54	49.50
Si K	70.46	50.50
Totals	100.00	

EDS Elemental analysis

Fig. 1. Photographs and surface microstructures of (a, c, e) ground bare graphite pebble and (b, d, f) CVR-SiC-coated graphite pebble prepared at 1750 °C (2 h).

analysis of the surface of the CVR-SiC-coated pebble showed practically the same atomic percent of carbon and silicon, 49.50% and 50.50%, respectively.

Fig. 2 shows high magnification FE-SEM images highlighting the surface morphology of the CVR-SiC-coated graphite pebbles. The surface of the CVR-SiC coating showed a relatively dense microstructural morphology consisting of crystalline grains closely bonded together, as typically observed in sintered ceramics. The surface of the CVR-SiC coating fabricated at 1850 °C (2 h), showed a denser morphology compared with that obtained at 1750 °C (2 h). It seems that such densification of the coating surface leads to an improvement in oxidation resistance and durability as well as in mechanical properties. During the CVR process, the conversion of SiC grains from graphite (coke) grains and the pitch source of the boundary region induces the bonding of constituent grains in the SiC coatings.

Fig. 3 shows the cross-section and microstructure of a polished and fractured pebble prepared by the CVR-SiC coating process. It was inferred that a SiC coating layer with a thickness of approximately 30 μm was formed over the entire surface of the graphite pebble by the conversion mechanism involving SiO vapor created during the CVR process. It is likely that the SiC coatings on the graphite pebbles possess a boundary pattern characterized by a composition gradient between the SiC phase and carbon source. The SiC coating on the graphite pebbles, as shown in the fractured specimen of Fig. 3(b), were observed to be very dense and uniform.

Fig. 4 shows the XRD pattern of CVR-SiC coating layers on a graphite pebble and cube. The XRD patterns of the surface of the prepared pebble and cube clearly indicated the presence of a SiC crystalline phase, with strong peaks corresponding to the (111), (220) and (311) planes. The XRD patterns of a crushed flake (Fig. 4(c)) of the coated pebbles, the ground graphite

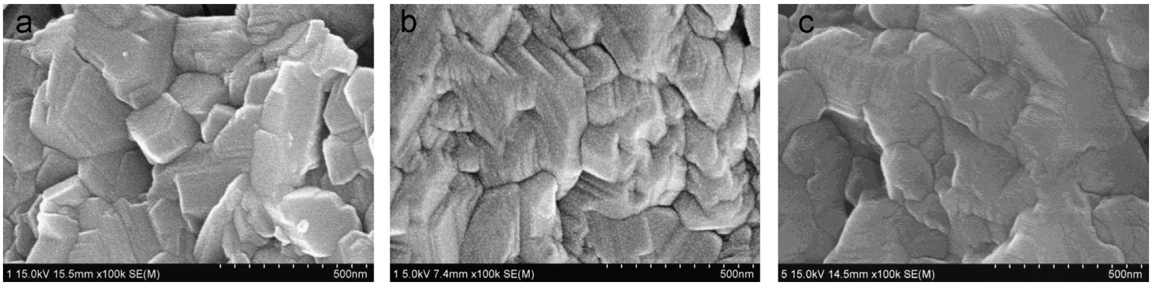


Fig. 2. Surface morphologies of CVR-SiC-coated graphite pebbles prepared (a) at 1750 °C (2 h), (b) at 1800 °C (1 h) and (c) at 1850 °C (2 h).

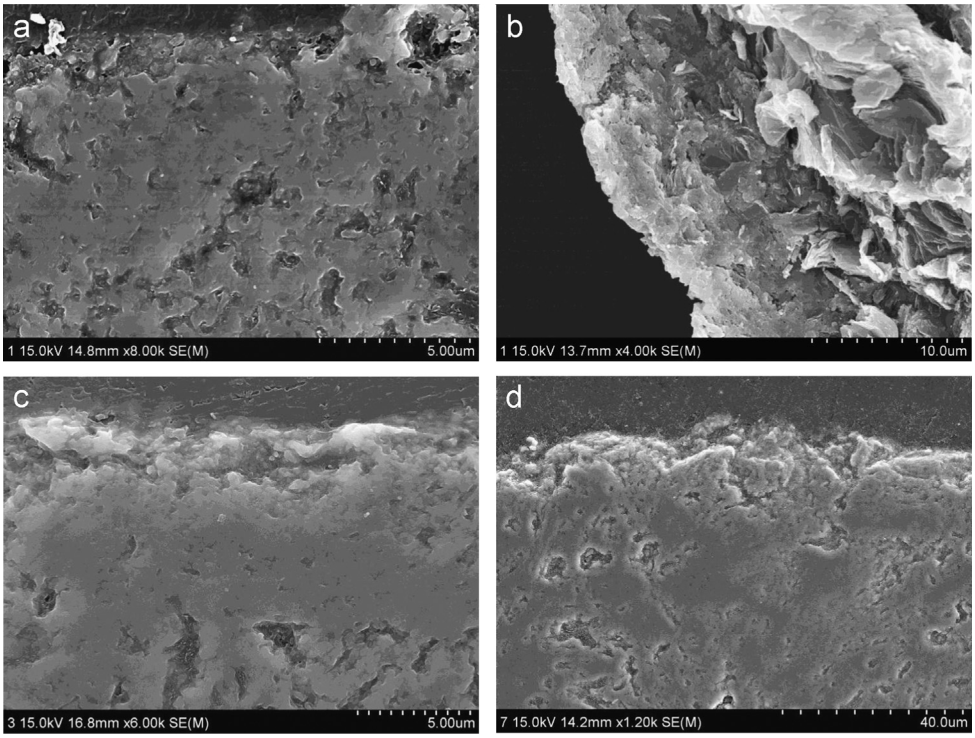


Fig. 3. Cross-sectional microstructure of CVR-SiC-coated graphite pebbles prepared at (a, b) 1750 °C (2 h), (c) 1800 °C (1 h), and (d) 1850 °C (2 h). (a, c, d) Polished specimen and (b) fractured specimen.

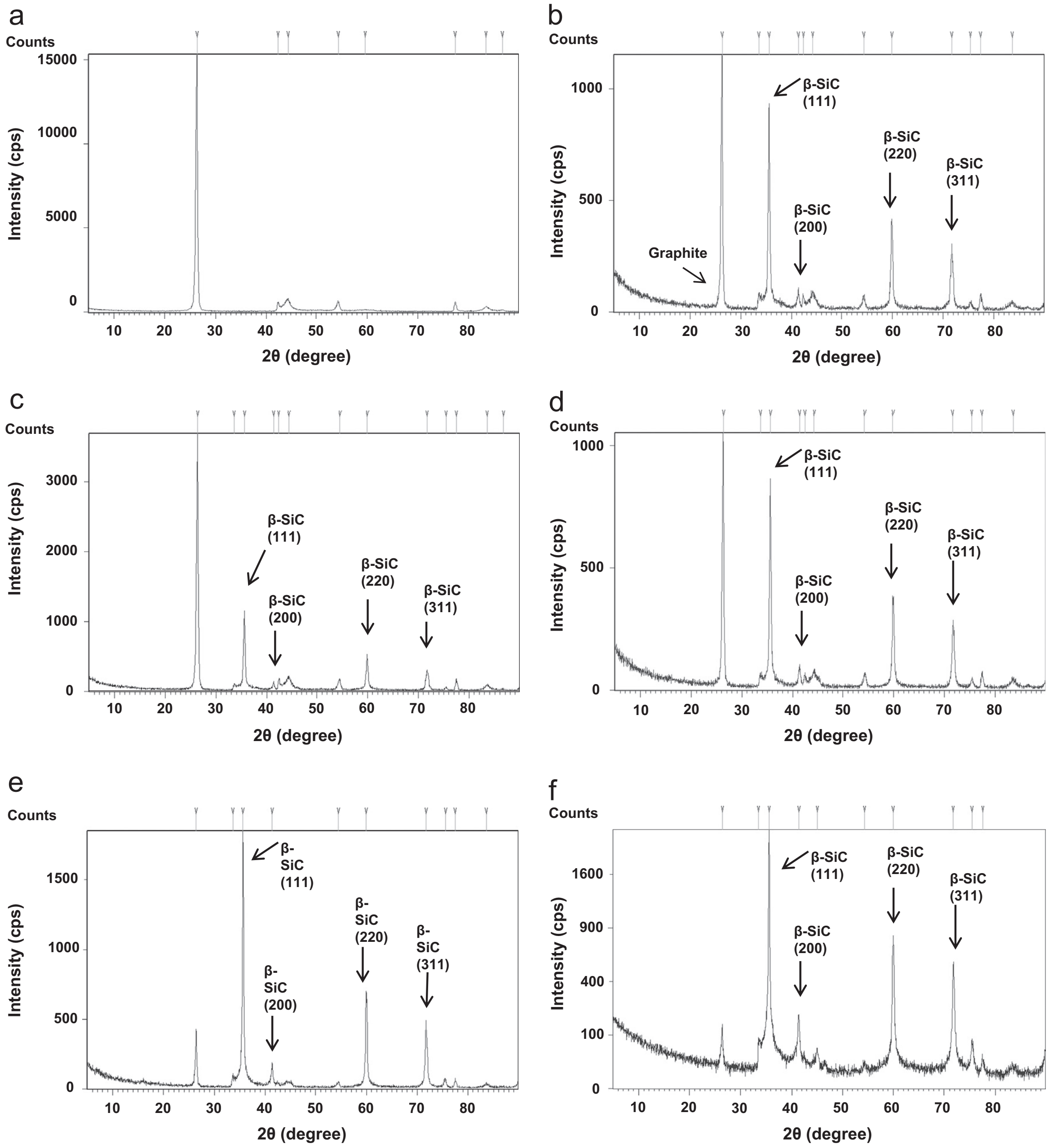


Fig. 4. X-ray diffraction patterns of (a) ground bare graphite cube (8 mm^3), (b) CVR-SiC-coated graphite cube (8 mm^3) prepared at 1750 °C (2 h), (c) crushed flakes of CVR-SiC-coated graphite pebbles (1750 °C, 2 h), (d) CVR-SiC-coated graphite pebble aggregates (1800 °C, 1 h), (e) CVR-SiC-coated graphite cube (2 mm^3) aggregates (1800°C, 1h) and (f) CVR-SiC-coated graphite cube (8 mm^3) (1850°C, 2 h).

cube (Fig. 4(a)) and coated pebble aggregates (Fig. 4(d)) were analyzed. The (111) peak intensity of the SiC coating on the graphite pebbles and cubes remarkably increased with the reaction temperature. In particular, the specimen (Fig. 4(f)), fabricated at 1850 °C (2 h), showed a very high peak intensity and a low graphite peak.

Fig. 5 shows the pore size distribution and the porosity of the CVR-SiC-coated graphite pebbles. The center of the major peak in the pore size distribution, measured by mercury intrusion porosimetry for the coated graphite pebble aggregates, shifted from 2 μm to nearly 1 μm in diameter. The most important change in the coated graphite pebbles was the notable decrease in the porosity of the pebbles following CVR coating. The porosity of the SiC-coated graphite pebbles decreased upon increasing the reaction temperature to 1850 °C (2 h). Such a decline in the porosity of the coated specimens is indicative of the densification of the pebble surfaces during the CVR process. The dense surface morphologies of the coated specimens, shown in Fig. 2, provide indirect evidence of the decrease in porosity (densification behavior) in the reaction zone near the pebble surface.

Fig. 6 shows the results of the oxidation and temperature difference experiments performed using a DSC/TGA instrument. The bare graphite pebble aggregates (Fig. 6(a)) were completely oxidized, showing a strong exothermic curve when exposed (at 700 °C) to air flow for less than 2 h. Although the

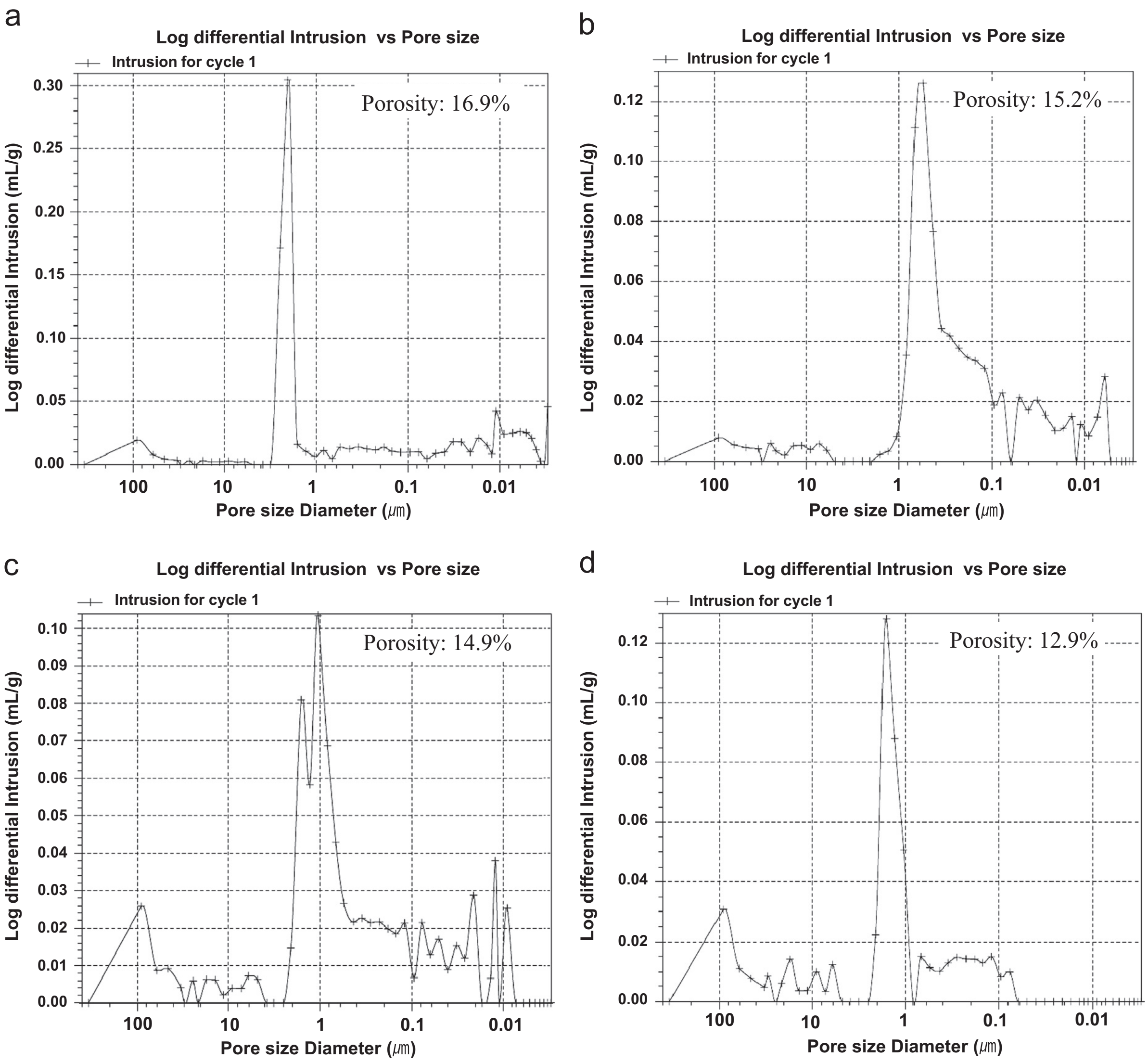


Fig. 5. Pore size distribution and porosity of (a) graphite pebble aggregates and CVR-SiC-coated graphite pebble aggregates prepared at (b) 1750 °C (2 h), (c) 1800 °C (1 h) and (d) 1850 °C (2 h).

coated graphite pebbles obtained at 1750 °C (2 h) and 1800 °C (1 h) showed a significant weight loss of 50 wt%, the specimen coated at 1850 °C (2 h) showed very low weight loss within 2–4%. The specimen (Fig. 6(d)) prepared at 1850 °C (2 h) using excess carbon was also analyzed. The SiC-coated graphite pebbles (Fig. 6(d) and (e)) showing low weight loss to air at elevated temperature presented slightly exothermic or endothermic behavior during the oxidation test. The oxidation resistance (low weight loss) observed at elevated temperature in air is considered to be directly related to the strong SiC peak intensity of the specimen coated at 1850 °C (2 h), as indicated by the specimen's XRD pattern as well as its quite low porosity, which was reduced from 16.9% before coating to 12.9% after coating.

In light of the above, the XRD peak intensity and the porosity are critical factors that determine the most suitable coating conditions and criteria required for quality control in fabricating CVR-SiC-coated graphite pebbles. It was demonstrated that SiC-coated graphite pebbles could be easily fabricated by the CVR process using a graphite furnace. It was also observed that the CVR process has the advantages of exploiting a simple chemical vapor reaction between silica and a carbon source and enabling the formation of uniform coatings on spherical pebbles without the complex equipment typically used in the CVD process. Currently, the Korean HCCR TBM team is conducting a development project to prepare a practical protocol for the mass production of the CVR-SiC-coated graphite pebbles.

4. Conclusions

SiC coatings were successfully formed over graphite pebbles by the CVR process for neutron reflector applications relevant to the Korean Helium Cooled Ceramic Reflector (HCCR) Test Blanket Module (TBM). Uniform SiC coating layers, showing strong XRD peaks for the (111), (220), (311) crystalline planes, were formed on graphite pebbles by the CVR process. FE-SEM images revealed the dense and fine-grained surface morphology of the CVR-SiC-coated graphite

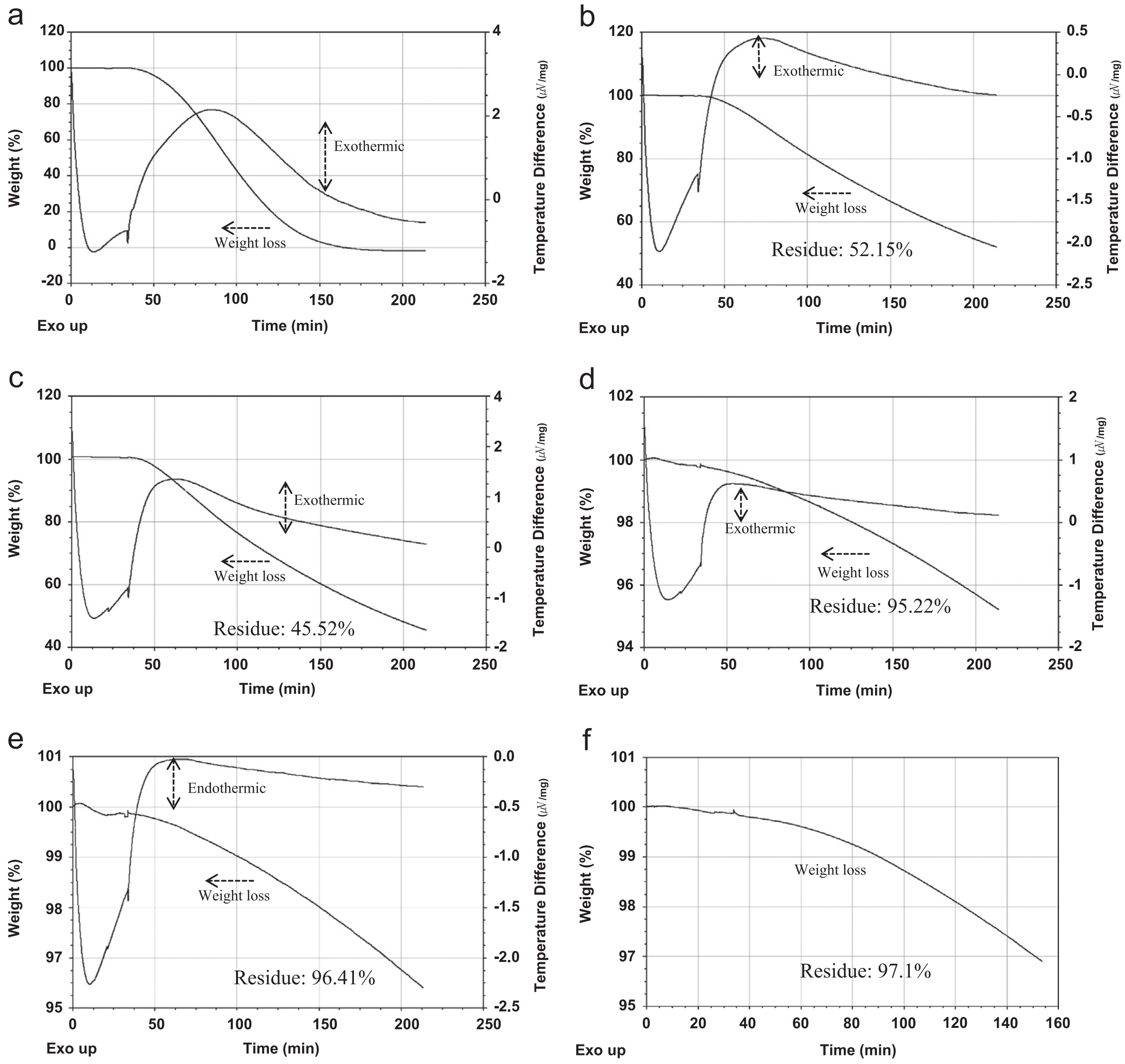


Fig. 6. DSC/TGA results for (a) graphite pebble aggregates and CVR-SiC-coated graphite pebble aggregates prepared at (b) 1750 °C (2 h), (c) 1800 °C (1 h), (d) 1850 °C (2 h) (with excess carbon), (e) 1850 °C (2 h) and (f) *1850 °C (2 h). (a–e)—air blowing (100 ml/min.). (f)—*air blowing (50 ml/min.).

pebbles. A SiC coating layer measuring approximately 30 μm in thickness was formed over the surfaces of the graphite pebbles by the CVR process. Before coating, the graphite pebbles showed a porosity of 16.9%; after coating, the porosity of the graphite pebbles decreased markedly to 12.9%. The CVR-SiC-coated graphite pebbles coated at 1850 °C (2 h) showed the lowest weight loss (within 2%). Our results regarding the CVR coating process suggest that SiC-coated pebbles can be mass-produced to create neutron reflectors for the HCCR TBM. Currently, the mass production process is being modified to create a new and better protocol.

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