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Journal of Nuclear Materials 281 (2000) 163–170

journal of nuclear materials

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Multi-layer coating of silicon carbide and pyrolytic carbon on UO_2 pellets by a combustion reaction

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Received 10 May 1999; accepted 1 July 2000

Abstract

The coating layers of silicon carbide and pyrolytic carbon on UO_2 pellets were prepared by using a combustion reaction between the carbon and silicon layers. The pyrolytic carbon and silicon were deposited by thermal decomposition of propane at 1250°C in a chemical vapor deposition unit and microwave pulsed electron cyclotron resonance plasma enhanced chemical vapor deposition (ECR PECVD) using silane at 500°C. Microstructural observation of the layers with scanning electron microscopy (SEM) showed that an inner layer existed following the surface contour of the pellet and the outer layer had a small number of fine pores inside. Chemical analyses with Auger electron spectroscopy (AES) and X-ray diffractometry (XRD) revealed that the inner and outer layers were pyrolytic carbon and silicon carbide, respectively. From the transmission electron microscopy (TEM) observation, the silicon carbide formed during the combustion reaction was identified as fine crystalline β-SiC. The temperature distribution of the specimen during the combustion reaction was estimated by a finite element method, which showed that preheating above 1300°C was required for the combustion reaction between silicon and carbon to propagate well through the specimen. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

The addition of a coating on the nuclear fuel, which has been introduced from the preparation of modular high temperature gas cooled reactor (MHTGR) fuel, is one of the methods to enhance the safety and to assure the highly reliable performance of such a kind of fuel [1]. Since the coating layers serve as a miniature container of fission products, a skeleton capable of withstanding external load and a barrier of cooling gas contamination under reactor operation, certain materials with desirable behaviors under neutron irradiation and with desirable microstructure and strength should be deposited on the nuclear fuel. In case of the fuels for the MHTGR, multi-layer of carbide and pyrolytic carbon was used as TRISO (four layers of porous pyrolytic carbon, dense pyrolytic carbon, dense silicon carbide or zirconium carbide (ZrC) and dense pyrolytic carbon) or BISO (a double layer composed of pyrolytic carbon) type. The inner porous microstructure was for retaining the fission gas released and the dense microstructure was for keeping the structural integrity and preventing radioactive products from migrating into the coolant during reactor operation [2,3]. It is well known that the multi-layer of inner porous carbon layer with equiaxed grains, β-SiC with fine columnar grains and the outer dense carbon layer with equiaxed grains is one of the optimum combinations of the coating layers on nuclear fuel for satisfactory performance of the coated fuels [1–3].

The microstructure of the coating layer depends on the coating process, shape and type of substrate materials, and coating parameters such as temperature and pressure [4]. For MHTGR fuels, the coating layer of pyrolytic carbon has been prepared by the thermal decomposition of hydrocarbons, such as methane,

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PII: S0022-3115(00)00365-2

acetylene and propane, and the coating layer of silicon carbide has also been produced by the chemical vapor deposition using methyltrichrolosilane at a high temperature above 1600°C [5]. Although the coating process for the light and particle shaped MHTGR fuels has been well established, a coating process for the heavy and cylindrical nuclear fuels has not been developed. Furthermore, it is necessary to develop a new coating process with the advantage of environmental safety to avoid the release of toxic gases by selecting different source gases, as well as with microstructural integrity by reducing the coating temperature.

Silicon carbide was produced by a combustion reaction between carbon and silicon because of its heat of formation of −67 kJ/mol [6,7]. The combustion reaction, so-called self-propagating high temperature synthesis (SHS), is a solid-state combustion process characterized by an exothermic heat release sufficient to propagate a combustion front through the powder compact; in the reaction the reactant powder is completely consumed once ignition is achieved. It has the advantages of highly pure products, economically rapid processing, the potential for non-equilibrium products and no high temperature furnace processing [8]. In the case of the formation of silicon carbide by a combustion reaction, additional heat was required to propagate the reaction front continuously due to its relatively low heat of formation.

Although a considerable amount of literature exists on the preparation of silicon carbide by the combustion reaction between carbon and silicon powders and the preparation of coating layers on particle shaped nuclear fuel by normal chemical vapor deposition techniques, little information is available on the methods of obtaining coating layers on the cylindrical UO_2 nuclear fuel pellet by a combustion reaction between carbon and silicon layers. Hence, the objectives of this study are to develop an innovative and safe coating process carried out at relatively low temperature using a combustion synthesis and to characterize the coating layers deposited on the cylindrical UO_2 pellets, which are fundamental to the feasibility study about the application of the coating process for the fuels of light water reactors (LWR) and heavy water reactors (HWR). Microstructural observation and chemical analysis of the layers were carried out by scanning electron microscopy (SEM), transmission electron microscopy (TEM), Auger electron spectroscopy (AES) and X-ray diffractometry (XRD), respectively. The temperature distribution of the specimen during the combustion reaction was estimated by a finite element method.

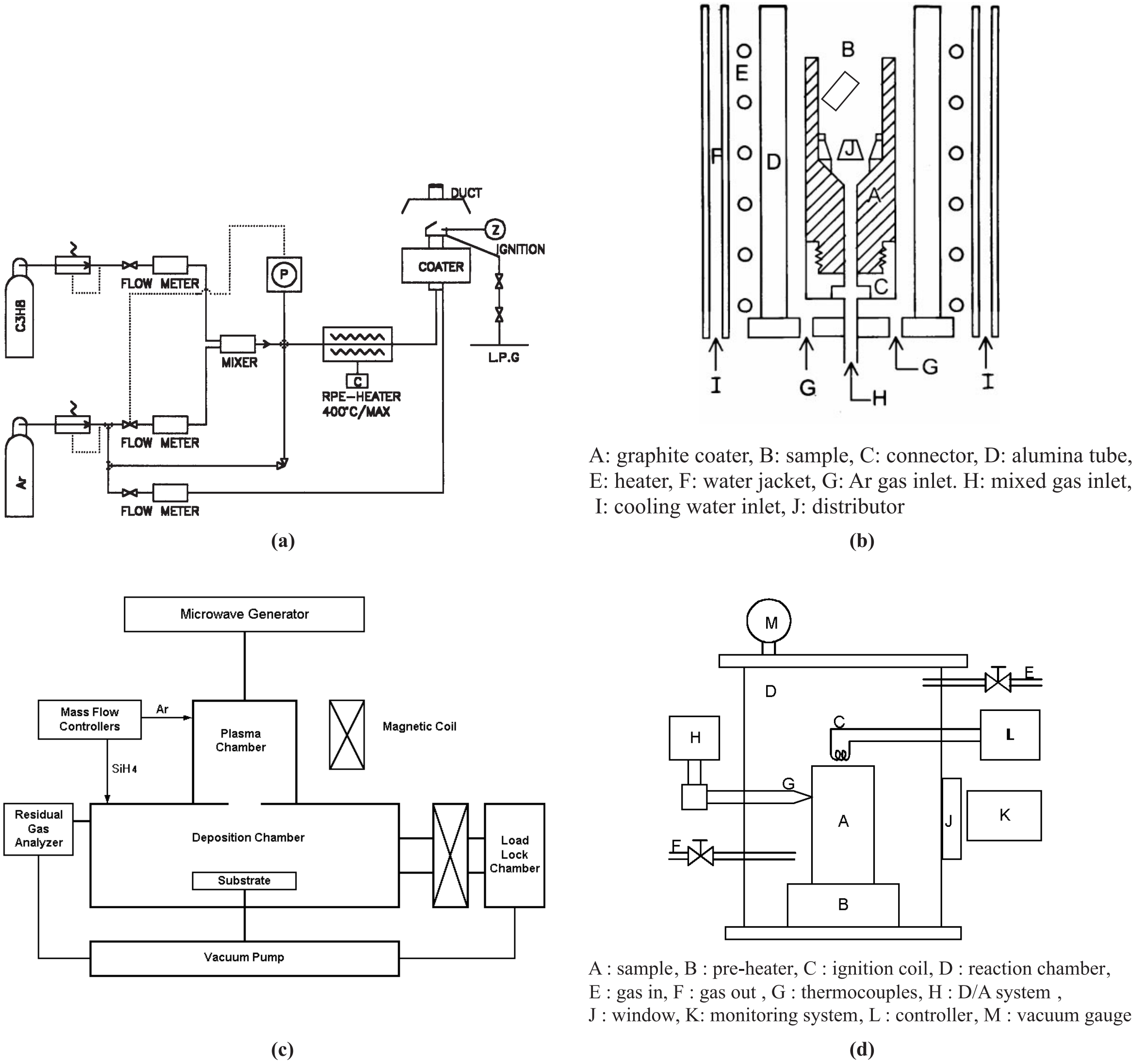
2. Experimental method

The cylindrical UO_2 pellets, about 10 mm in diameter and about 12 mm in height, were prepared by pressing uranium dioxide powder into cylindrical shape and sintering it. The pellets were coated after surface treatment. Three experimental apparatuses were used: a fluidized bed type chemical vapor deposition (FBT CVD) unit for pyrolytic carbon coating, a microwave pulsed electron cyclotron resonance plasma enhanced chemical vapor deposition (ECR PECVD) unit for silicon coating and a combustion chamber for the combustion reaction between silicon and carbon for the preparation of silicon carbide layer. Fig. 1(a) shows the schematic diagram of the carbon deposition unit, which consists of a 1500 kW resistance furnace, a preheater of the source gases, a gas mixer, a temperature controller, and a gas flow control system. Inside the furnace, a coater with a cone angle of 60° and 300 mm in length is installed as shown in Fig. 1(b). The total gas flow during the experiment was maintained constantly by a gas flow meter and a mass flow controller. Propane (99.9%) and argon gases were used as a carbon source and a carrier gas, respectively. The total pressure in the coating chamber was 1 atm. The samples were installed in the graphite coater with four channels in which each sample was located and floated by gas passing through a nozzle and a distributor. The deposition was carried out at 1250°C by thermal decomposition of propane. A gas mixture initially consisting of 25% propane and 75% argon was preheated to 400°C before the thermal decomposition in the coater. Table 1 shows the coating conditions of pyrolytic carbon.

After deposition of pyrolytic carbon on the pellet, silicon was deposited with silane gas (SiH_4) on the layer of pyrolytic carbon by a ECR PECVD unit. Fig. 1(c) shows the schematic diagram of the ECR PECVD which contains a three-dimensional coating stage inside. The coating conditions of silicon employed in this study are in Table 2. The coating process was carried out at the base pressure of 10^{-6} Torr and 500°C. The magnetic field was supplied by use of a magnetic coil around the periphery of the plasma chamber during deposition. Argon gas as a carrier gas and silane gas as a source gas were introduced into the plasma chamber and the deposition chamber, respectively [9,10].

A combustion reaction between silicon and carbon was carried out in a combustion chamber by igniting reactant layers with a heating coil after preheating above 1200°C. Fig. 1(d) is the schematic diagram of a combustion chamber. During the reaction, the combustion behavior was observed with a video camera through the windows. After the combustion reaction, pyrolytic carbon was deposited on the SiC coating layer in some sample.

The phase identification of the coated layers was performed by AES (VG 2400) and XRD (Rigaku). The microstructure of each layer was observed by SEM (Jeol 6400) and TEM (Jeol 200 CX). In order to determine the preheating effect on the combustion reaction, the internal



(a)

A: graphite coater, B: sample, C: connector, D: alumina tube, E: heater, F: water jacket, G: Ar gas inlet. H: mixed gas inlet, I: cooling water inlet, J: distributor

(b)

(c)

A : sample, B : pre-heater, C : ignition coil, D : reaction chamber, E : gas in, F : gas out , G : thermocouples, H : D/A system , J : window, K: monitoring system, L : controller, M : vacuum gauge

(d)

Fig. 1. Schematic diagrams of (a) the carbon coating apparatus, (b) the fluidized bed coater, (c) ECR PECVD unit and (d) SHS chamber.

Table 1
Coating conditions of pyrolytic carbon

Deposition temperature (°C)	1250
Total flow rate (ℓ/min)	1.5–2.0
Composition of source gas (%)	25
Total weight of specimen installed (g)	80
Size of each sample (mm)	Dia. 10
Pre-heating temperature (°C)	400
Cone angle of coater (°)	60
Size of coater (mm)	I.D. 50 × 300
Cone angle of distributor (°)	60
Size of distributor (mm)	I.D. 23 × 20
Nozzle size of distributor (mm)	1.0

Table 2
Deposition conditions of a Si film by ECR PECVD

Parameter conditions	Conditions
Pressure and base pressure (Torr)	10^{-4}–10^{-7}, 2×10^{-6}
Substrate temperature (K)	298
Microwave power (W)	300
Pulse on time and period (μs)	17–100, 33–200
Microwave frequency (GHz)	2.45
Microwave flux density (G)	875
Substrate distance form plasma chamber (cm)	15

temperature distributions under various preheating conditions were estimated numerically by a finite element method.

3. Results and discussion

3.1. Microstructural observation of the coating layers

Fig. 2 shows the photographs of UO_2 pellets without and with coating layers, where the surface of the cylindrical pellet after coating lost luster. The coating layers on the pellet consist of inner pyrolytic carbon layer, middle silicon carbide layer formed by a combustion reaction and outer pyrolytic carbon, as shown in Fig. 2(b). Fig. 3 is the cross-sectional view of a coated pellet observed by SEM. As shown in Fig. 3, uniform coating layers consisting of pyrolytic carbon and silicon carbide formed by a combustion reaction between pyrolytic carbon and silicon, and pyrolytic carbon coating in that order were obtained on the pellet following the surface contour with the average total thickness of about 100 μm. Fig. 4(a) is scanning electron micrograph of the double layer formed by the combustion reaction between the pyrolytic carbon and silicon layers. Fig. 4(b) is the Auger spectra of the outer layer prepared by the combustion reaction between the pyrolytic carbon and

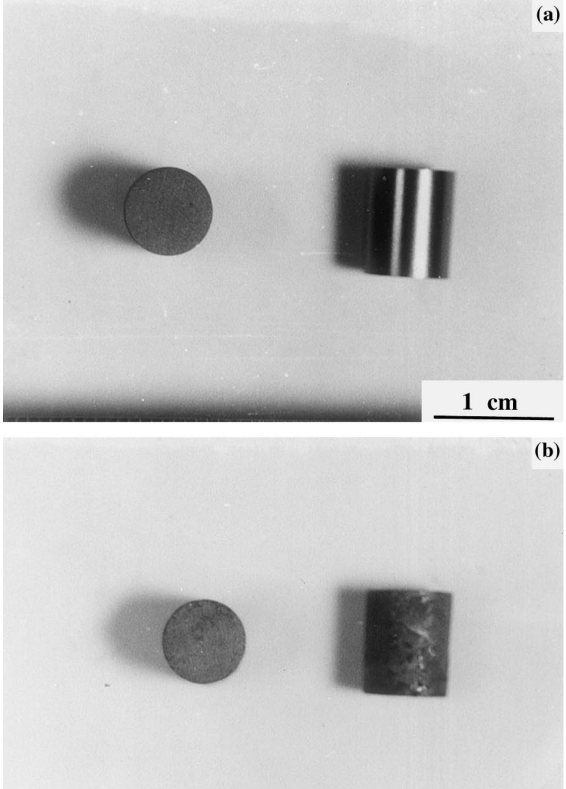


Fig. 2. Photographs of UO_2 pellets: (a) as-received; (b) C/SiC/C coated.

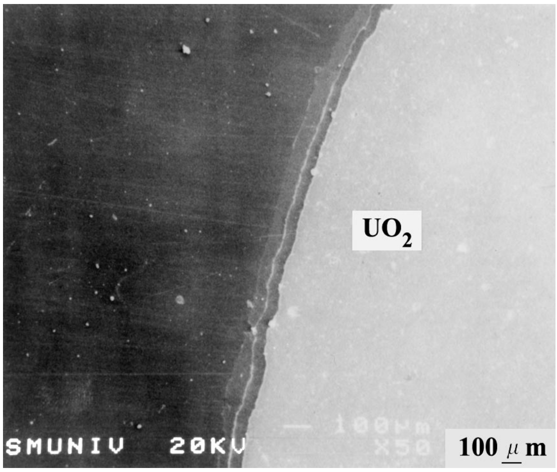


Fig. 3. SEM images of a cross-section of C/SiC/C multi-layer coated UO_2 pellet.

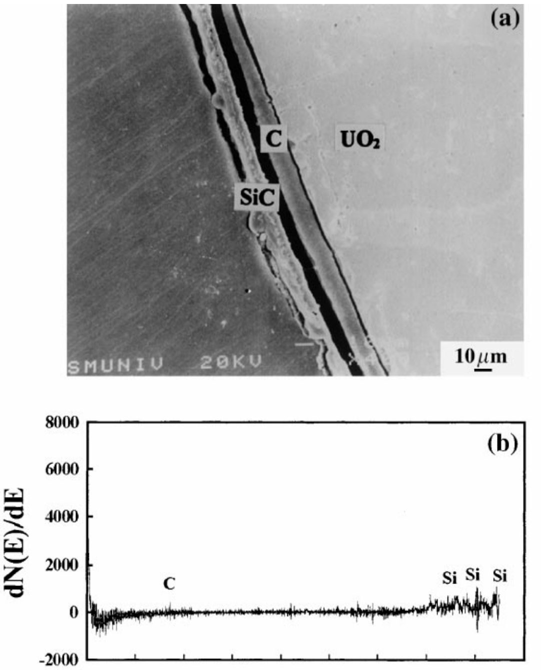


Fig. 4. SEM image and AES spectra of C/SiC coating layers: (a) SEM image; (b) AES spectra.

silicon layers. Fig. 5 shows the XRD spectra of reactant (top) deposited by ECR PECVD after coating of pyrolytic carbon by FBT CVD and the combustion product (bottom) formed by the reaction between silicon and carbon. The X-ray spectra showed that the reactant is silicon and carbon, and the product is mainly β-SiC with small amount of unreacted silicon. This is in agreement with previous study [7,11]. Accordingly, chemical analysis of AES and XRD supported that the inner and outer coating layers were pyrolytic carbon and silicon carbide, respectively.

Fig. 6 is a cross-section of the layers consisting of pyrolytic carbon and silicon carbide formed by a combustion reaction between pyrolytic carbon and silicon, and pyrolytic carbon coating in that order. This illustrates a multi-coating layer on the UO_2 pellet. Fig. 7 is a high magnification of the cross-section of the coated pellet. As shown in this figure, the inner pyrolytic carbon layer has fine, equiaxed grains and the silicon carbide

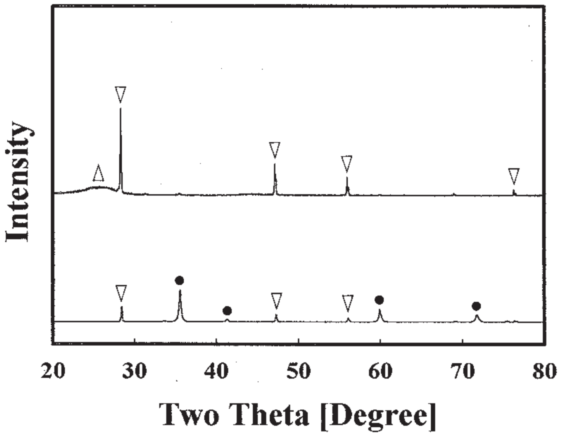


Fig. 5. XRD spectra before and after combustion reaction. (△) C; (▽) Si; (●) β-SiC.

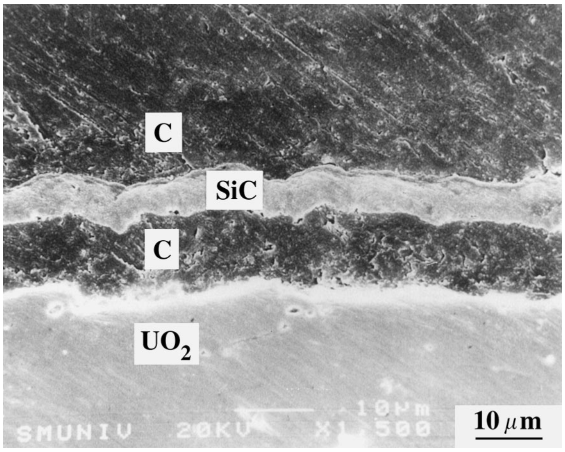


Fig. 6. Scanning electron micrograph of a cross-section of C/SiC/C multi-layer coated UO_2 pellet.

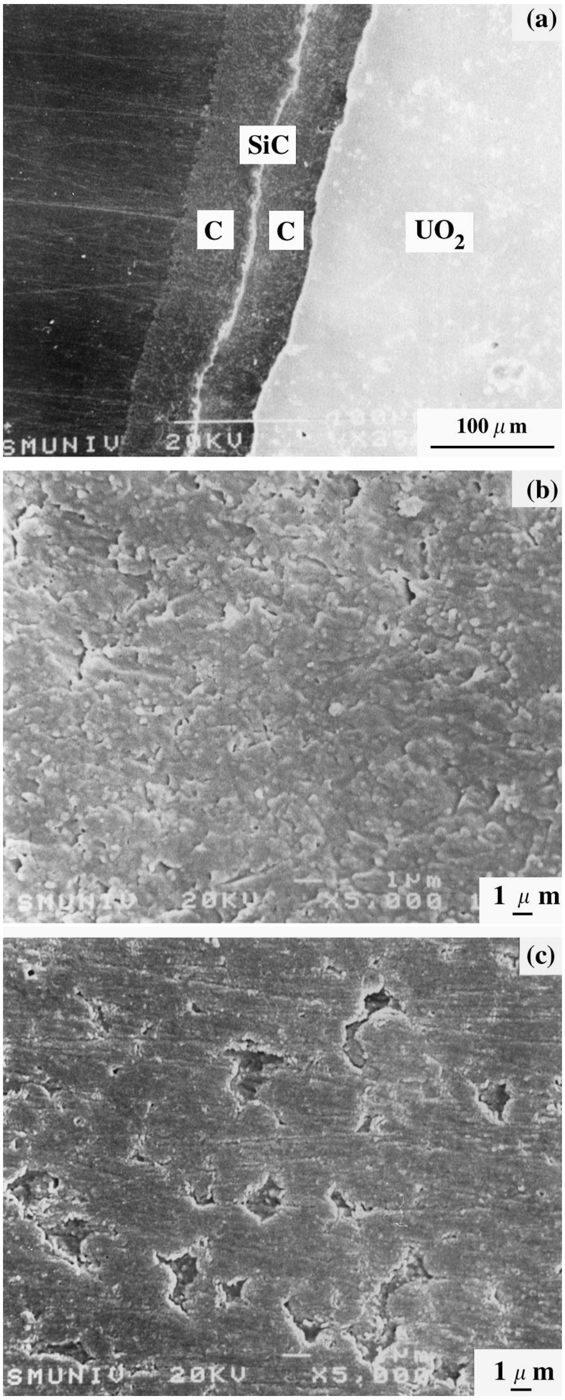


Fig. 7. High magnification of scanning electron micrographs of a cross-section of a coated UO_2 pellet: (a) cross-section (250×); (b) inner layer (5000×); (c) middle layer (5000×).

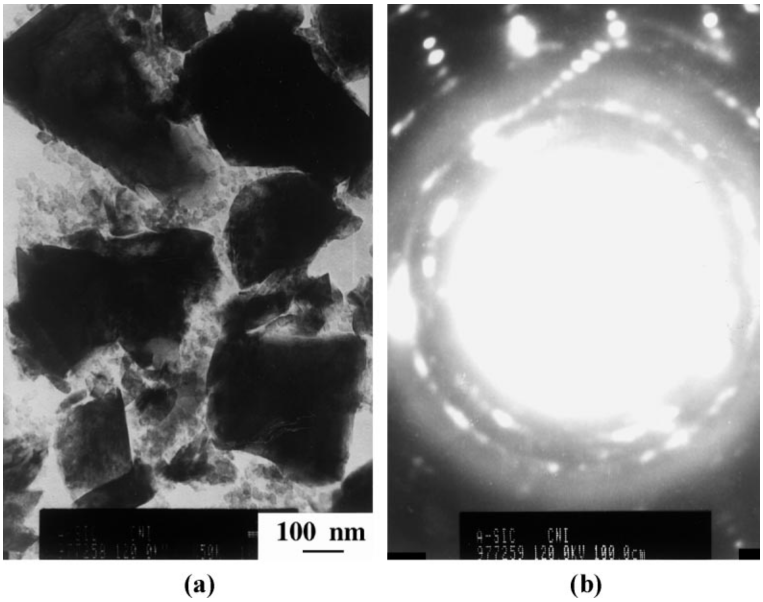


Fig. 8. TEM image of a coating layer: (a) bright field; (b) diffraction pattern.

layer in the middle has a relatively dense structure with a small number of pores inside, which seem to have been introduced during the combustion reaction. Fig. 8 is a TEM image of the coating layer. The sample was prepared by scratching the middle layer followed by slightly pulverizing its debris. As shown in the bright field image and diffraction pattern, the silicon carbide formed by the combustion reaction between silicon and pyrolytic carbon layers is fine grained β-SiC. Hence, preparation of uniform and homogeneous multi-coating layer of pyrolytic carbon and silicon carbide on cylindrical UO_2 pellets is possible by using a combustion reaction between pyrolytic carbon and silicon prepared by chemical vapor deposition at a relatively low temperature.

3.2. Estimation of preheating effect on the temperature distribution during a combustion reaction

Since the energy of formation for SiC is not enough to self-propagate, it is necessary to estimate the required preheating temperature. In this study, the required preheating temperature was estimated by numerical modeling based on empirical observations in previous study [11]. The combustion reaction was able to propagate with a certain preheating of the specimen. Although a one-dimensional model of the combustion reaction under a steady state condition was well deliberated, little information about a three-dimensional model has been available [12–16]. An estimation of the three-dimensional temperature distribution during the combustion reaction was numerically attempted by finite element method, in which the assumptions are as follows:

1. combustion reaction moves in a certain single direction,
2. specimen is homogeneous and has isotropic properties,
3. heat transfer coefficient is constant,
4. amount of evaporation is negligible,
5. heat loss to surrounding environment is negligible, and
6. heat transfer during the reaction occurs by conduction and convection.

The governing equation describing the reacting system under the above assumptions is

$$\rho c\left(\frac{\partial T}{\partial t}+[v]^{\mathrm{T}}[L]T\right)+[L]^{\mathrm{T}}[q]=\ddot{q}, \tag{1}$$

where ρ is the density, c the specific heat, T the temperature, t the time, $[L]$ the vector operator, $[v]$ the velocity vector for mass transport of heat, $[q]$ the heat flux vector, and $\ddot{q}$ is the heat generation rate per unit volume. For the heat flux vector to the thermal gradient, Fourier's law gives the following equation:

$$[q]=-[D][L]T, \tag{2}$$

where, $[D]$ is the conductivity matrix. Combining Eqs. (1) and (2), gives

$$\rho c\left(\frac{\partial T}{\partial t}+[v]^{\mathrm{T}}[L]T\right)-[L]^{\mathrm{T}}([D][L]T)=\ddot{q}. \tag{3}$$

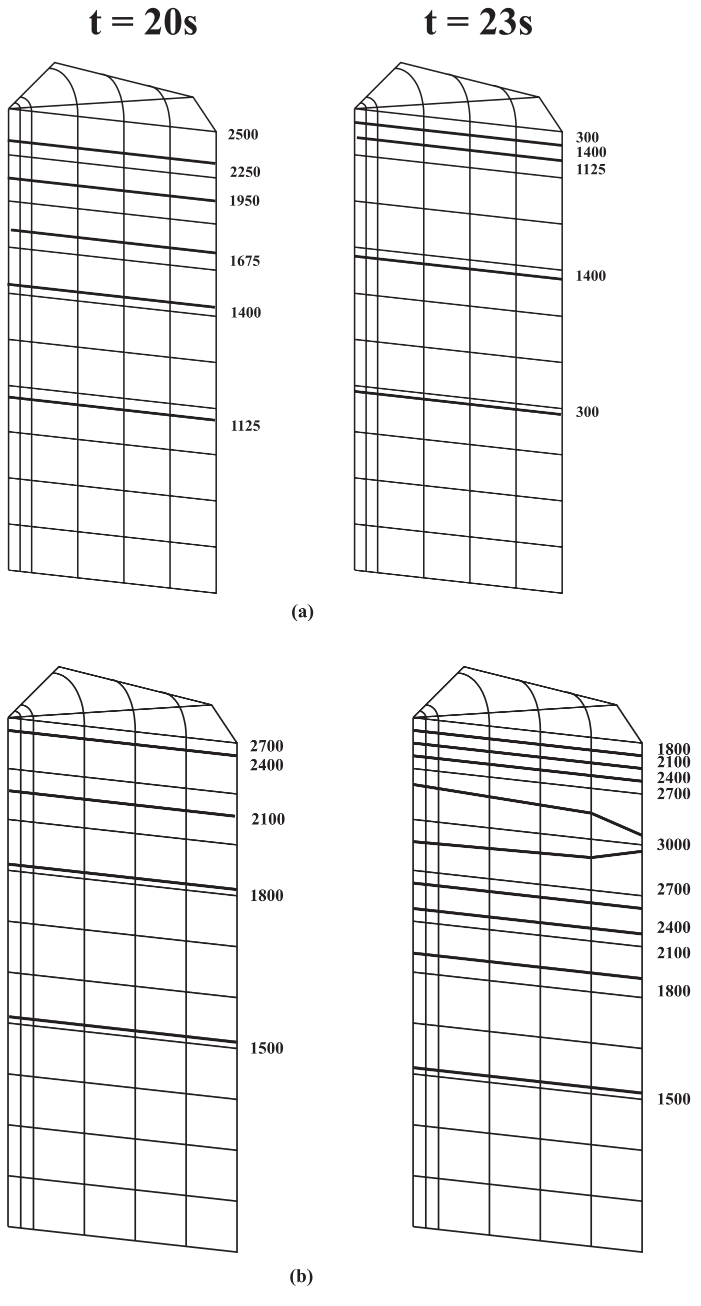
Integrating Eq. (3) for the entire volume, we obtain the equation

$$\int_{\mathrm{vol}}\left(\rho c\delta T\left(\frac{\partial T}{\partial t}+[v]^{\mathrm{T}}[L]T\right) - [L]^{\mathrm{T}}([D][L]T)\right)\mathrm{d(vol)} = \int_{\mathrm{vol}}\delta T\ddot{q}d(V)+\int_{\mathrm{suf}}\delta T h_{\mathrm{f}}(T_{\mathrm{B}}-T_{\mathrm{S}})\,\mathrm{d}S. \tag{4}$$

For the global cartesian system with radius R, it is assumed that initial and boundary conditions are as follows:

1. $0 < R < 1,\ 0 < \theta < 2\pi,\ z = 0,$
2. $0 < R < 1,\ 0 < \theta < 2\pi,\ z = 10,$
3. $R = 1,\ 0 < \theta < 2\pi,\ 0 < z < 10,$

where T is the heating temperature, $\delta T/\delta t$ the initial temperature, $[q]^{\mathrm{T}}[\eta] = -h_{\mathrm{f}}(T_{\mathrm{B}} - T_{\mathrm{S}})$, $[\eta]$ the unit outward



(a)

(b)

Fig. 9. Estimated temperature distributions of the specimen ignited by a 2500°C heater with various preheating temperatures: (a) 300°C; (b) 1300°C (left–time step = 20 s, right–time step = 23 s).

normal vector, h_f the film coefficient, T_B the bulk temperature and T_S is the surface temperature.

There are usually three temperatures to describe combustion behaviors such as adiabatic temperature, combustion temperature and ignition temperature. The adiabatic temperature is the ideal maximum temperature due to the exothermic heat of the combustion reaction. The combustion temperature is the real combustion temperature, which is always equal to or lower than the adiabatic temperature without any addition of extra-heat. The ignition temperature is the temperature at which a combustion reaction begins. The adiabatic temperature of the combustion reaction between silicon and carbon powders is known as 1527°C [17]. In order to self-propagate the combustion reaction through the specimen under the preheating condition, it should be at a high temperature such as adiabatic temperature for the time being. The ignition temperature in this calculation was arbitrarily selected considering the tungsten heater and adiabatic temperature of the reaction. Fig. 9 presents the estimated temperature distributions of the specimen ignited by a 2500°C heater with different initial temperatures. The adiabatic temperature of the silicon carbide formation by the reaction between silicon and carbon is reported as about 1527°C. Combustion temperature is dependent upon combustion condition, which is lower than adiabatic temperature. As shown in Fig. 9(a), the higher temperature region than the adiabatic temperature of about 1527°C was not formed after 20 s and the temperature of the sample more decreased after 23 s. This means that the exothermic heat due to the formation of silicon carbide is not enough to completely propagate combustion wave through the sample at the preheating temperature of 300°C. However, as shown in Fig. 9(b), the higher temperature region than the adiabatic temperature of about 1527°C formed after 20 s and the temperature of the region increased after 23 s. It means that the exothermic heat due to the formation of silicon carbide under the 1300°C preheating condition is sufficient for the combustion flame to pass through the specimen completely. This numerical estimation suggests that 1300°C preheating is required for the combustion reaction between silicon and carbon. In this study, we estimated temperature profile of the specimen with 50°C temperature interval from 0°C and obtained 1300°C.

4. Conclusions

1. Multi-layer of silicon carbide and pyrolytic carbon on the cylindrical UO_2 pellets were homogeneously deposited following the surface contour with the average thickness of about 100 μm by the combustion reaction between the silicon and carbon layers.
2. AES, XRD and SEM revealed that the inner and outer coating layers were pyrolytic carbon with fine and equiaxed grains and relatively dense silicon carbide, respectively. The silicon carbide formed by the combustion reaction between silicon and pyrolytic carbon layers was β-SiC.
3. Preparation of a uniform and homogeneous multi-layer coating of pyrolytic carbon and silicon carbide on the cylindrical UO_2 pellet is possible using a combustion reaction between pyrolytic carbon and silicon produced by chemical vapor deposition at relatively low temperatures.
4. Empirical observation and numerical analysis showed that preheating above 1300°C is required for the combustion front to propagate through the silicon and carbon mixture to produce silicon carbide.

Acknowledgements

The authors would like to express their appreciation to the Ministry of Science and Technology (MOST) of the Republic of Korea for the support of this work through the mid- and long-term Nuclear R&D Project. One of authors thanks 1999 Sunmoon University Foundation.

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