

Microstructure and mechanical properties of chemical vapor deposited ZrC film on SiC/graphite substrate

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Both ZrC and SiC layers are crucial layers in TRISO coated fuel particles since they prevent diffusion of fission products and provide mechanical strength for the fuel particle. However, each layer has its own defects, so the purpose of this study is to determine such defects in these layers. In this study, we carried out thermodynamic simulations before actual experiments. With these simulation results, we deposited the ZrC layers on SiC/graphite substrates through a CVD process. SiC films on graphite have different microstructures which are a hemispherical angular, domed top and faceted structure at different deposition temperatures. According to the microstructures of SiC, the preferred orientation, hardness and elastic modulus of deposited ZrC layers are changed. New combinations of coated ZrC/SiC/graphite were made to improve mechanical properties and chemical properties for the purpose of fabricating TRISO coated fuel particle with high stability.

Key words: SiC, ZrC, Preferred orientation, Microstructure, Mechanical property.

Introduction

Tristructural isotropic (TRISO) coated fuel particles are one of the most important materials for hydrogen production using high temperature gas-cooled reactors (HTGR). It is composed of three isotropic layers; an inner pyrolytic carbon (IPyC) layer, a silicon carbide (SiC) layer and an outer pyrolytic carbon (OPyC) layer to retain fission products inside the fuel particle. Among the coated layers, the SiC layer is the most essential layer for TRISO coated fuel particles as it prevents diffusion of metallic and gaseous fission products and provides mechanical strength for the fuel particle [1-5]. However, SiC has a critical disadvantage that it loses mechanical integrity by thermal dissociation and a phase change. As a result, the ability of the SiC layer to capture fission products such as cesium decrease at a high temperature. Due to this defect, a zirconium carbide (ZrC) layer has been considered instead of the SiC layer. ZrC has a higher melting point of 3,400 °C and a higher temperature stability than SiC. In addition, ZrC has a higher resistance to chemical attack by fission products than SiC. However, ZrC also has its own defects in that the mechanical strength of ZrC is weaker than SiC. In

order to solve all these problems, we deposited a ZrC layer inside the SiC-TRISO coated fuel particles. The ZrC layer deposited on the SiC layer may improve the mechanical strength and protect the OPyC layer against metallic and gaseous fission products [6, 7, 8].

In this study, we used a horizontal CVD system which has several advantages such as good uniformity and high purity when depositing ZrC at high temperature and high pressure. To apply the CVD system, we obtained the best deposition conditions for ZrC through a thermodynamic simulation (SOLGASMIX-PV program). With these simulation results, we characterized the properties of deposited ZrC on SiC/graphite substrates.

Experimental procedure

We calculated equilibrium compositions of the condensed phase ZrC, other condensed phases and gas phases at thermodynamically equilibrium conditions as functions of temperature, pressure, and input gas ratio using the SOLGASMIX-PV program. ZrC/SiC films were deposited in a horizontal hot wall tube furnace. The horizontal CVD system with a super kanthal furnace is shown in Fig. 1. Zirconium chloride (ZrCl₄) and CH₄ were used as a source for ZrC deposition. The TG/DTA analysis data of ZrCl₄ powder showed that its melting temperature was 238 °C. Therefore, ZrCl₄ powder was sublimated at near the sublimation temperature using a source heating system. Ar gas was used as a carrier gas and H₂ was a

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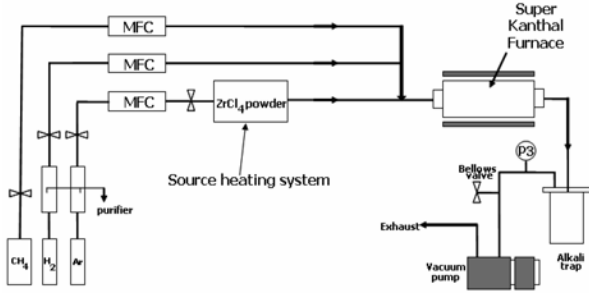


Fig. 1. Schematic diagram of the super kanthal furnace CVD system.

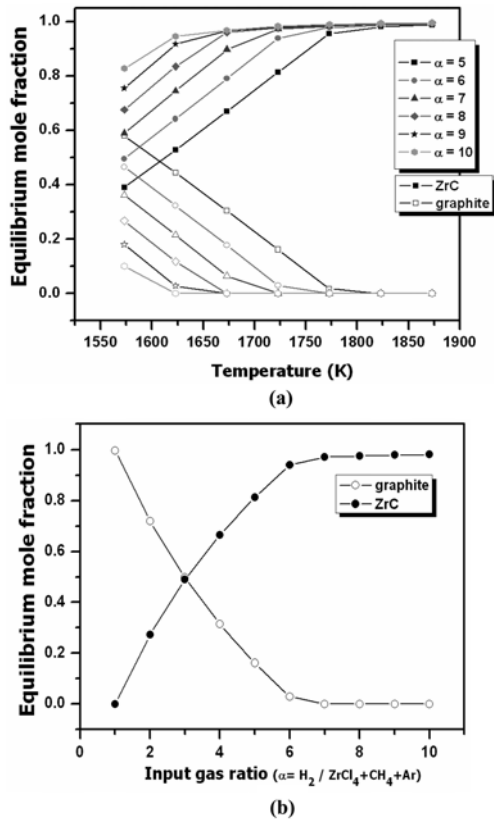


Fig. 2. Thermodynamic yield of ZrC layer as function of deposition parameters which is based on (a) temperature and (b) input gas ratio at 1400 °C. (Closed and open symbols represent yields of ZrC and graphite for the given α (input gas ratio) and deposition temperature, respectively.)

diluent gas to control the concentration of the mixture of zirconium chloride vapor. The flow rate was controlled by a mass flow controller (MFC). The input gas ratio of diluent gas to ZrCl_4 plus CH_4 gas plus carrier gas ($\alpha = P_{\text{H}_2} / P_{\text{ZrCl}_4 + \text{CH}_4 + \text{Ar}}$) was 10 and total gas flow rate was fixed at 5000 sccm according to the simulation results while total pressure was fixed at 684 torr (0.9 atm).

A SiC inter-layer in the ZrC/SiC/graphite specimen was chemically vapor deposited on the isotropic graphite substrate which has a similar thermal expansion coefficient to that of SiC in order to improve adhesion property of SiC to the substrate. For the ZrC deposition, we used SiC as a substrate deposited in the range of temperature from

1,100 °C to 1,300 °C since SiC has different microstructures as a variation of deposition temperature. The SiC deposited at 1,100 °C has a hemispherical angular structure with small grains, the surface morphology deposited at 1,200 °C has a stratified domed top structure with a high corrosion resistance plane and the SiC deposited at 1,300 °C has a faceted columnar structure [9, 10, 11, 12].

In order to investigate the phase and preferred orientation of deposited ZrC layers, the X-ray diffraction (XRD) method was used. The microstructures of deposited ZrC layers on each substrate were examined using scanning electron microscopy (SEM). To measure the hardness and elastic modulus of deposited ZrC films, we used a nano-indenter (Nantester, MicroMaterials, Wrexham, UK) with a Berkovich indenter in the indentation load range from 10 to 100 mN.

Results and discussions

Fig. 2 shows the thermodynamic yield of condensed phases which were calculated by SOLGASMIX-PV thermodynamic computer program. Equilibrium compositions of ZrC obtained a yield over 80% when the input gas ratio was above 6 and the deposition temperature was above 1,400 °C. Comparing with ZrCl_4 and CH_4 , the higher H_2 rate and deposition temperature are, the higher yield of ZrC we obtained. Based on these results, we performed a CVD ZrC process under the condition of $\alpha = 10$ and 1,400 °C.

Fig. 3(a) shows the X-ray diffraction results of ZrC layers deposited at 1,400 °C on three different microstructures of SiC films on graphite substrates. Three different types of sub-deposited SiC layer which have different microstructures of hemispherical angular structure, domed top and faceted structure were used as substrates [9, 10, 11, 12]. Hereafter, we refer to deposited ZrC layers on hemispherical angular, domed top and faceted structure SiC as Z1, Z2 and Z3, respectively. Since all the X-ray patterns present (111), (200), (220), (311), (222) and (400) planes, deposited ZrC films are identified as ZrC with the face centered cubic (FCC) structure. Z1, Z2, and Z3 have a strong (200) preferred orientation regardless of the sub-deposited layers. On the other hand, when we compared (111) and (220) of the secondary X-ray peak planes of these specimens, the intensity of the (220) plane was higher than the (111) plane for the Z1 and Z2 samples. However, for Z3, the intensity of the (220) plane decreased more than for the (111) plane. To confirm this phenomenon, we calculated numerical values of the texture coefficient and the results are shown in Fig. 3(b). A texture coefficient (T.C) using the Harris method was adopted to observe the relative degree of preferred orientation among crystal planes as follows [13];

$$TC(hkl) = \frac{I_{(hkl)} / I_{o(hkl)}}{\frac{1}{N} \sum (I_{(hkl)} / I_{o(hkl)})}$$

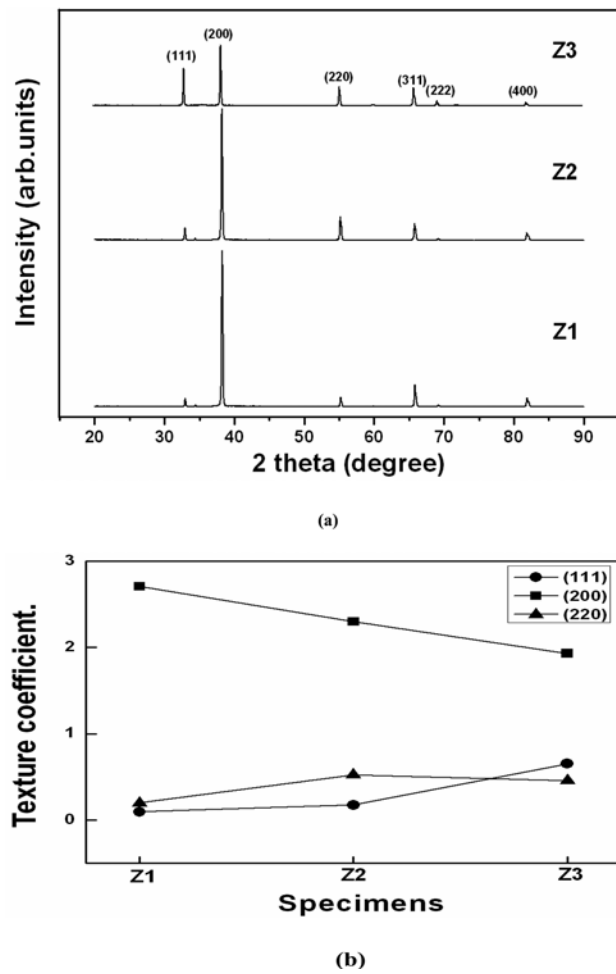


Fig. 3. (a) XRD patterns and (b) texture coefficients of ZrC films deposited on three different microstructures of SiC films on graphite substrates. ($T = 1400^\circ\text{C}$, $\alpha = 10$, 0.9 atm)

where, $I_{(hkl)}$, $I_{0(hkl)}$ and N are the measured intensities of the film, the standard integrated intensities of powdered ZrC and the number of reflections, respectively. As shown in Fig. 3(b), the preferred orientation in all the ZrC films are the (200) plane. The texture coefficient of the (220) plane was a little higher than the (111) plane for the Z1 and Z2 samples. In the Z3, sample the texture coefficient of the (111) and the (220) was opposite to that of Z1 and Z2. It seems that this also depends on the different morphology of the sub-deposited SiC layers. As a result of the analysis of XRD patterns and texture coefficients with different substrates, deposited ZrC films have a preferred orientation of the (200) plane and the secondary peak was changed from the (220) to (111) depending on the microstructure of SiC.

Fig. 4 a', b', c' shows the surface microstructures of Z1, Z2 and Z3. The surface microstructure of the Z2 sample showed columnar grains with the domed top structure and this seems to follow the microstructure of the sub-deposited SiC layers. The Z3 specimen was a faceted columnar structure and large cones constituted the surface of the films. The ZrC of both Z2 and Z3 specimens were deposited with the same tendency of

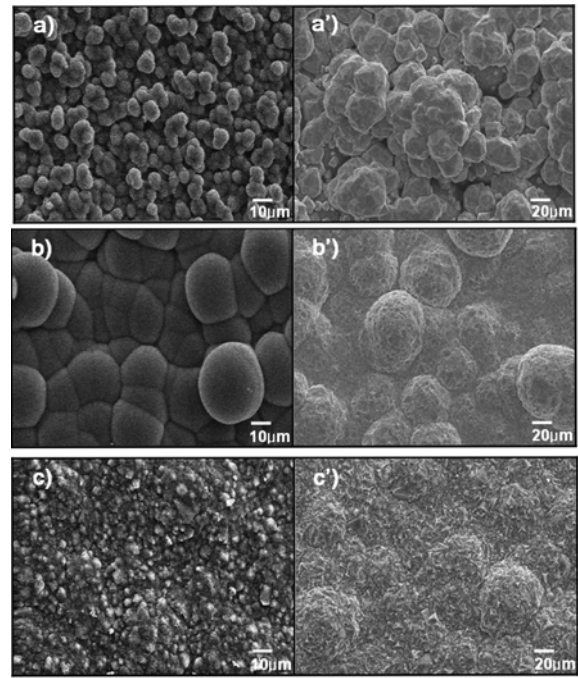


Fig. 4. Surface morphologies of the ZrC films deposited at 1400°C ($\alpha = 10$, 0.9 atm) according to the microstructure of the sub-deposited SiC layers < a) hemispherical angular b) domed top and c) faceted SiC layer on graphite, then, a'), b') and c') are three corresponding microstructures of Z1, Z2, and Z3, respectively >

sub-deposited layer. However, the microstructure of the deposited Z1 sample does not follow well that of the sub-deposited SiC layer. The deposited ZrC showed an hexagonal formed columnar structure which was different from the hemispherical angular structure of the sub-deposited layer. In addition, the deposited ZrC film on Z1 showed a more porous and less densely populated structure. Generally, carbide materials deposited on graphite substrates by CVD are polycrystalline and their microstructure has been found to strongly depend on the deposition temperature. However, in our experiments with the same deposition temperature, the change of microstructure seems to depend on the surface growth trend caused by the microstructure of the sub-deposited layer. Therefore, a sub-deposited layer effect must be considered before following layer deposition in the case of deposited multi-layers.

Fig. 5 shows the mechanical property changes of ZrC films with different microstructures on Z1, Z2, and Z3 specimens. Other research about the mechanical properties of ZrC showed that the hardness of ZrC is in the range of 22-24 GPa, with an elastic modulus of approximately 355 GPa [14]. In our nanoindentation measurements of Z1, Z2 and Z3 specimens, the hardnesses of each specimen were 32.41, 34.09 and 35.80 GPa, respectively. In general, the mechanical properties of polycrystalline materials are affected by many factors such as grain size, pore size, phase distribution and preferred orientation [15]. Thus, deposited ZrC films with the same preferred orientation

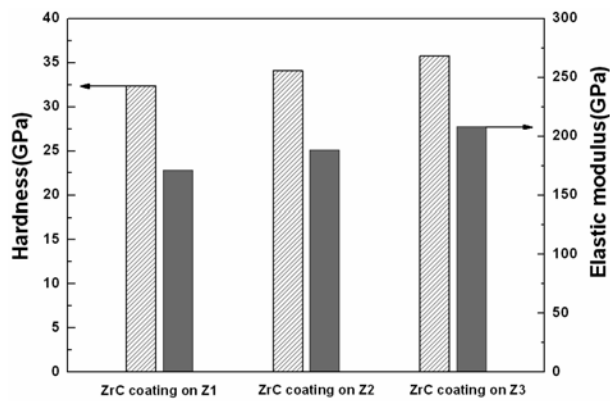


Fig. 5. Hardness and elastic modulus of ZrC coating films on various substrate. (hemispherical angular, domed top and faceted, respectively)

of (200) plane, have different hardnesses and elastic moduli values due to other factors. Since the ZrC films of Z1 were more porous and a less densely populated structure, the hardness value of Z1 was the lowest. In the case of Z3, the hardness value was larger than Z2 due to having the smallest grain size and the highest intensities of the (111) plane. Since the (111) plane is the close packed plane of ZrC, a higher preferred orientation of the (111) plane improves the mechanical properties of ZrC. The elastic modulus values of deposited film showed a similar tendency to the hardness values. The elastic modulus value of Z3 was the largest at 208 GPa. The elastic modulus values of Z1 and Z2 were 171 GPa, 197 GPa, respectively. Measurement results of mechanical properties of ZrC shows that the ZrC deposited on the SiC substrate with a faceted structure has higher hardness and elastic modulus values than the ZrC deposited on SiC substrates with hemispherical angular and domed top structure. Compared with results of other research, the hardness of deposited ZrC is higher and the elastic modulus is lower than values in the literature [14]. In our experiment, these results are thought to reflect that the morphology of the sub-deposited SiC layer has an effect on the properties of deposited ZrC.

Conclusions

We deposited ZrC on SiC with three different microstructures by a hot wall type CVD reactor using ZrCl_4 and CH_4 gas as source gas based on the results of

simulation data. Deposited ZrC films on sub-deposited SiC with the different microstructures were ascertained as ZrC with a (200) preferred orientation by XRD. However, the intensities of (111) and (220) planes of the secondary peak were changed due to the microstructure of the sub-deposited SiC. The microstructure of the ZrC films on Z2 and Z3 followed the microstructure of the sub-deposited SiC. However, the ZrC film on Z1 deposited on hemispherical angular type SiC was hexagonal formed columnar structure which is different to the sub-deposited layer. Measurement of mechanical properties using a nano-indenter showed that the hardness and elastic modulus of the deposited ZrC on the faceted structure has the highest value due to the effect of a smaller grain size, less porosity and more intense (111) peak which is the most densely populated plane. We identified that the surface morphology and mechanical properties of ZrC are changed by the microstructure of the sub-deposited SiC. In this study, we deposited ZrC films on SiC substrates with various microstructures. The ZrC film coated on a faceted structure SiC showed better properties than ZrC coated on other structures of SiC for the application of new TRISO coating materials.

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