

Fabrication of ZrC-TRISO layer on the ZrO₂ Particle using the Chloride Process

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1. Introduction

One of the promising methods in the hydrogen production is nuclear technologies based on the use of VHTR. These reactors are being under development and should provide a core-output He temperature at a level of 1000°C. To realize this requirement, the present R&D of materials programs on VHTR are emphasized on development of metallic materials for the core as well as on advanced fuel development and tests. The development of advanced coated fuel particles with the use of ZrC instead of SiC is needed because SiC has good properties for a TRISO fuel, however, it gradually loses its mechanical integrity at very high temperatures, above 1700°C, by a thermal dissociation. Zirconium carbide (ZrC) is well known as a refractory and chemically stable compound, with a melting point of 3540°C. Therefore, ZrC could have a higher resistance to a chemical attack by fission product elements such as Pd and Cs and it is reported that ZrC is a better barrier for Cs than SiC by post-irradiation heating experiments [1]. For this reason, ZrC has been focused on for replacing the material of the SiC layer in the TRISO coating layers, and many researchers have reported ZrC coating methods with various Zr-salts-CH₄ as a source material for fluidized bed chemical vapor deposition (FBCVD) equipment [2-5]. Among these methods, a chloride process is a preferred process because of its less hazardous and better stoichiometric composition than the other processes.

KAERI has been developing ZrC-coated fuel particles as an advanced particle. In this study, coating technique of ZrC on the surface of the ZrO₂ particle by chloride process has been developed. The purpose of the present work is to investigate the coating conditions and deposition parameters of ZrC coatings on their composition and some characteristics.

2. Experimental Procedure

Prior to an experiment, an equilibrium composition of the ZrCl₄-CH₄-Ar-H₂ system to establish a reasonable deposition condition was calculated by using SOLGASMIX-PV, a widely used computer program for calculating an equilibrium state in a chemical system [6]. Through the calculation, experimental conditions were settled on as input gas ratios ($\alpha = [H_2/(CH_4+ZrCl_4)]$) of 5, a source gas ratio in the input gas ($\beta = [Zr/(Zr+C)]$) in the input gas) of 0.8, a total

system pressure of 10 torr, and deposition temperatures of 1400°C. ZrCl₄ powder (Aldrich Co. 99.9%) and CH₄ was used as source materials, and H₂ acted as a reducing agent gas for the ZrCl₄ vapor. To investigate the sublimation property of the ZrCl₄ powder, a DTA-TG analysis was carried with an inert atmospheric condition, temperature range from RT to 500°C, and a heating rate of 1°C/min. ZrC TRISO coating was deposited in a fluidized bed on ZrO₂ particles using gas mixtures of ZrCl₄, CH₄, Ar and H₂. We used an internally designed vaporizer and crucible of ZrCl₄ for a constant supply of the ZrCl₄ vapor to the reactor by a carrier gas. The ZrC were deposited on ZrO₂ particles at temperature of 1400–1600°C with 50°C intervals in a 1" graphite tube. The crystal structure of the ZrC layer was investigated by x-ray diffraction (XRD) analysis. The microstructure of the ZrC was observed by SEM (JEOL, JSM5200), and the homogeneity of the ZrC were evaluated with EDS in the mode of a line scanning.

3. Results and Discussion

The thermodynamic calculation by SOLGASMIX-PV is useful method to establish the equilibrium gas composition and thermodynamic yield. This program can be calculate the equilibrium condition in the systems containing a gaseous phase, condensed phase solutions, and condensed phases of invariant and variable stoichiometry. For our considering systems of ZrCl₄-CH₄-Ar-H₂, the database contains the Gibbs energy coefficients for the 40 ~ 44 gaseous compounds and for the 9 condensed stoichiometric phases. According to the thermodynamic calculation results, the stoichiometry of ZrC was likely to be improved with increasing α , β and the temperature. High value of β means that a larger amount of ZrCl₄ gas is needed to form ZrC than that of CH₄ due to the reactivity difference between the Zr and C containing gas species.

Figure 1 shows the DTA-TG results, which was analyzed with a heating rate of 1°C/min in an Ar atmosphere. The weight change curve shows sublimation behaviors of the ZrCl₄ powder with an increasing temperature. It seems that the sublimation of ZrCl₄ starts at 260°C with a high endothermic heat flow and it is nearly saturate at 285°C. The rapid drop of the weight change rate from 260°C to 285°C reflects a high evaporation rate in this temperature regime because the evaporation rate is directly related with a weight change at a fixed heating rate.

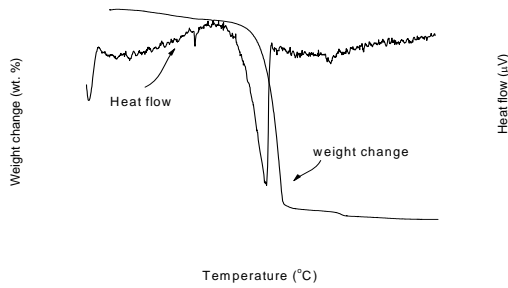


Fig. 1. TG-DTA result of the $ZrCl_4$ powder with a ramping rate of $1\text{ }^\circ\text{C}/\text{min}$

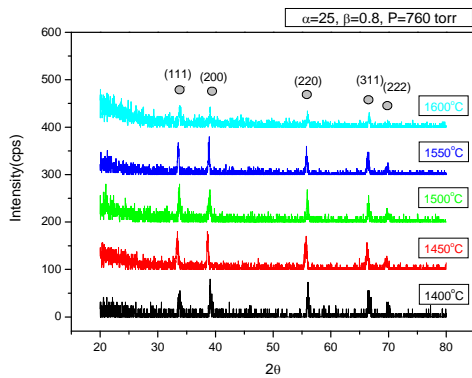


Fig. 2. XRD patterns of the ZrC layer with various deposition temperatures

Figure 2 shows a typical XRD patterns obtained on the coating layer of the microsphere with various deposition temperatures from $1400\text{ }^\circ\text{C}$ to $1600\text{ }^\circ\text{C}$. The XRD showed that all of the ZrC peaks corresponded to cubic ZrC in the JCPDS 35-0784. The ratios between the intensities of the peaks are about the same as those of the ASTM powder pattern. Some of the ZrC layers were oriented in the direction of (200) at $1400\text{ }^\circ\text{C}$. Five ZrC-TRISO samples at each deposition temperature were carried out. The average thickness of coated ZrC layers was $24.40\text{ }\mu\text{m}$ at $1400\text{ }^\circ\text{C}$, $29.00\text{ }\mu\text{m}$ at $1500\text{ }^\circ\text{C}$ and $25.00\text{ }\mu\text{m}$ at $1600\text{ }^\circ\text{C}$, respectively.

Figure 3 represents the appearance of the coating layer and microstructure of ZrC-TRISO coated layer on a ZrO_2 sphere deposited at $1500\text{ }^\circ\text{C}$. The sphere has been coated with a low density pyrolytic carbon (buffer) made using acetylene and dense IPyC, and the thin light-colored layer(ZrC) deposited between IPyC and OPyC. At the deposition temperature of $1500\text{ }^\circ\text{C}$, Almost all of grains for ZrC layer change to a larger grain or combined together like a snow crystal and the surface morphology of the ZrC was a large four fold grain and the fracture surface structure also changed to a wider column mixed with some isotropic or equiaxed crystallite shapes. At a high temperature, a fast grain growth could occur because enough energy for the

reaction is supplied to the sphere and it is delivered to the adsorbed atoms.

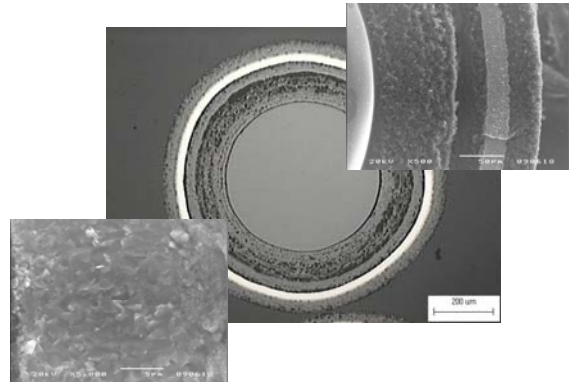


Fig. 3. TRISO-coated particle and magnified section of ZrC coated layer

4. Conclusion.

The influence of composition of vapor-gas mixture, containing $ZrCl_4$, methane, hydrogen and argon, on composition, structure and rate of coatings formation at depositing them on ZrO_2 spheres in a fluidized bed was investigated.

Thermodynamic calculations for the $ZrCl_4\text{-CH}_4\text{-Ar-H}_2$ system have made it possible to determine stable deposition conditions. Based on the thermodynamic calculations, a deposition of the ZrC was carried with various temperatures.

The stoichiometric ZrC was obtained at a temperature of $1500\text{ }^\circ\text{C}$ which was predicted by the thermodynamic calculation. The fracture morphologies of the ZrC layer were also showed with the deposition temperature.

REFERENCES

- [1] D. A. Petti, J. T. Maki, J. Buongiorno, R. R. Hobbins, G. K. Miller, Key Differences in the Fabrication, Irradiation and Safety Testing of U.S. and German TRISO-Coated Particle
- [2] K. Ikawa, J. Less-Common Metals, 29 (1972) 233-239.
- [3] P. Wagner, L.A. Wahman, R.W. White, C.M. Hollabaugh and R.D. Reiswig, J. Nucl. Mater., 62 (1976) 221-228.
- [4] T.Ogawa, K. Ikawa and K. Iwamoto, J. Nucl. Mater., 97 (1981) 104-112.
- [5] K. Ikawa and K. Iwamoto, J. Nucl. Sci. Tech., 11 (1974) 263-267.
- [6] T.M. Besmann, ORNL/TM-5775 (1977).