



# Deposition of ZrC-coated particle for HTR with ZrCl<sub>4</sub> powder

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## ABSTRACT

As the most promising candidate of SiC-coated fuel particles used in HTR fuel element, ZrC-coated particle has excellent irradiation performance. In this paper, ZrC coating is deposited by CVD with ZrCl<sub>4</sub> powder supply method. ZrCl<sub>4</sub> powder supply equipment and the saturation vapor pressure are studied, which show that saturation vapor pressure of ZrCl<sub>4</sub> is enough to satisfy deposition of ZrC coating in fluidized bed. Several deposition parameters such as C/Zr ratio and deposition temperature are investigated theoretically and experimentally, which have influence on ZrC coating key properties, such as mol ratio of Zr/C, and density. The results show that in a given temperature, C/Zr ratio in raw gas has more influence on ZrC structure, and high quality ZrC coating can be deposited by optimal condition with this method.

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## 1. Introduction

The coated fuel particle is the basic unit in spherical fuel element of high temperature gas cool reactor (HTR). Current HTRs use Triso-coated fuel particles which consist of pyrocarbon (PyC) and siliconcarbide (SiC) layers with a spherical fuel kernel. The SiC coating layer has a successful performance in irradiation test and experimental HTR running, as the primary load bearing shell which provides mechanical strength and main safety for coated particle.

For the future higher temperature in HTR, and better safety of HTR, new coating layers are studied to meet the demands; ZrC is one of the candidates with excellent performance in irradiation test (Ogawa et al., 1992; Bullock and Kaae, 1983; Reynolds et al., 1976; Minato et al., 1995; Minato et al., 1997). In previous studies (Chernikov and Kosukhin, 2006; Basini et al., 2008; Katsuichi Ikawa and Kazumi Iwamoto, 1974; Fukuda et al., 1975; Reynolds, 1974; Wagner et al., 1976; Hollabaugh et al., 1977; Ogawa et al., 1981), ZrC coating deposition, properties and microstructure, irradiation performance are investigated. Various fluidized bed, particles loading batch, and deposition parameters are adopted in the past work to product good quality ZrC coatings (ZrC-coated particles) and new attempts are still being conducted. Here the research works on ZrC coating are discussed in Institute of Nuclear Energy Technology (INET).

## 2. Experiment and results discussion

### 2.1. Experiment

The ZrC coating is deposited by chemical vapor deposition (CVD) method in a fluidized bed with a  $\varnothing$ 55 mm diameter inner tube. The fluidized bed is showed in Fig. 1. Deposition loading is about 50–80 g/batch, particles used in deposition is pre-coated buffer layer (about 95  $\mu$ m) and IPyC layer (about 40  $\mu$ m) on the ZrO<sub>2</sub> kernel (mean diameter  $\varnothing$ 500  $\mu$ m). ZrCl<sub>4</sub> powder, C<sub>3</sub>H<sub>6</sub>, H<sub>2</sub> and Ar are employed as react materials and carrier gas respectively.

Coated particles surface and section plane are observed with optics microscope and scanning electron microscope (SEM). Density is an important character of ZrC coating layer, here, ZrC coating layer density is measured by mass-volume measurement method. Three batch samples are extracted from one loading, ZrC piece of coated layers is peel from coated particles, and the pieces of one batch sample is measured three times. Deviations of each batch sample data to the mean value are less than 0.6%.

### 2.2. Precursor and apparatus in CVD deposition

Precursor supply of Zr-source is the most important technology in ZrC coating layer CVD deposition, because ZrCl<sub>4</sub> supply decides ZrC coating layer density and microstructure. So many methods are studied in order to provide a controllable and stable Zr-source to fluidized bed during ZrC deposition. The reaction of Zr-metal and halogen gas (Cl<sub>2</sub>, Br<sub>2</sub> and I<sub>2</sub>) is widely used in previous studies (Katsuichi Ikawa and Kazumi Iwamoto, 1974; Ogawa et al., 1981). Here we try to use a mixture method with powder supply and evaporation. The supply apparatus is composed of a mechanical helix feeder and an evaporation vessel. ZrCl<sub>4</sub> powder is fed by a

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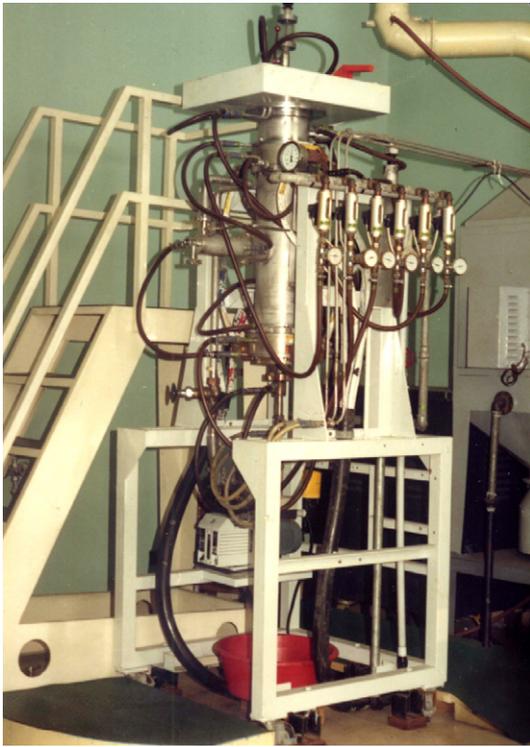


Fig. 1. Photo of fluidized bed with a  $\varnothing 55$  mm diameter inner tube.

mechanical helix (Hollabaugh et al., 1977; Chunbiao Du, 1996) and transported to an evaporation vessel, where  $ZrCl_4$  powder evaporated and enters into fluidized bed accompanied with carrier gas by a pipe. The pipe is heated and kept at a proper temperature above  $ZrCl_4$  condensing temperature. By controlling helix supply, heater temperature and transport gas flow,  $ZrCl_4$  vapor is controlled exactly and provides enough Zr-source for deposition.

Vapor pressure and evaporation rate are important for deposition rate and inner pressure of fluidized bed, when  $ZrCl_4$  powder enters into evaporation vessel, the evaporation rate should be quick enough to meet the transport gas flow, and vapor pressure should be high enough to meet fluidized bed inner pressure.  $ZrCl_4$  vapor pressure is tested from room temperature to  $400^\circ C$ , which includes the evaporating point of  $ZrCl_4$ , an enough high vapor pressure (Liu et al., 2007; Liu et al., 2008a,b) is measured during test temperature by the apparatus as showed in Fig. 2.

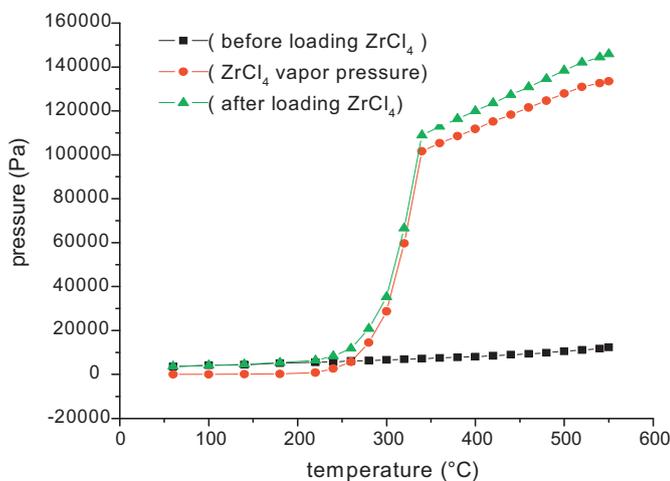


Fig. 2.  $ZrCl_4$  vapor pressure in evaporation vessel.

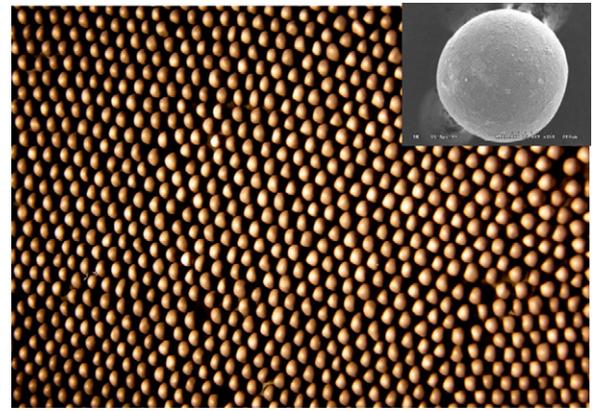


Fig. 3. Macro-photograph of ZrC-coated particles in a batch (the insert is photo of one ZrC-coated particle).

### 2.3. Deposition factors and results

For CVD deposition in a fluidized bed, many parameters, such as deposition temperature, gas composition, gas pressure and flow, have effect on both the chemical reaction and fluidization state. High quality coating layer needs a good fluidization behavior in a proper temperature zone. All particles in a batch are expected to be in equable quality, especially the coated particles manufactured in a large scale. For the given loading particles, the total gas flow, pressure could vary in a little range to meet the demand of fluidization and deposition condition. For a small batch deposition, it is easy to get a good fluidization.

In this work, effects of several parameters on ZrC coating properties and structure are studied, as done in other research works (Chernikov and Kosukhin, 2006; Basini et al., 2008; Reynolds, 1974; Wagner et al., 1976; Hollabaugh et al., 1977), deposition temperature and gas ratio (marked as C/Zr atomic ratio in gas) are compared. As usual, some properties and microstructure of ZrC-coated particles are studied. Fig. 3 shows the macro-photo of part of ZrC-coated particles in a batch. Fig. 4 is a section photograph of one ZrC-coated particle. Coated particles surfaces vary with different deposition conditions, surface is smooth with a low C/Zr ratio in gas, matte with a high temperature. Section photograph also shows the particles surface.

ZrC exists from  $1000^\circ C$  to  $2000^\circ C$  in Zr–C phase diagram, but the proper deposition temperature is higher than  $1200^\circ C$  in order to get a high density layer and proper deposition rate. Here ZrC coating deposition temperature is selected from  $1450^\circ C$  to  $1650^\circ C$  for the purpose of comparing temperature effect. A high deposition temperature is propitious to get a fast deposition rate, dense microstructure and high density, but too high deposition will lead to a large grain size, which is not good for ZrC strength. Fig. 5 shows ZrC coating layer density increases with deposition temperature, but decreases at  $1650^\circ C$ , because more codeposition of carbon leads to the reduction of density. Temperature also has an effect on CH gas pyrolysis, chemical equilibrium of C–H, and the synthesis of C–Zr chemical equilibrium. So, a high quality layer needs a proper temperature with given gas pressure, gas flow and given particles amount. It should be pointed out that deposition temperature discussed here is not an absolute temperature value, for different fluidized bed, the infrared meter may bring an error because of the measurement site and the instrument accuracy.

Except deposition temperature, Zr/C ratio in raw gas affects ZrC layer properties and microstructure greatly. In Fig. 5, two data lines show that less C/Zr in gas leads to a higher ZrC coating density at the same deposition temperature. Here we discuss two C/Zr atomic ratios: one is in raw gas and the other is in coating layer. C/Zr ratio in

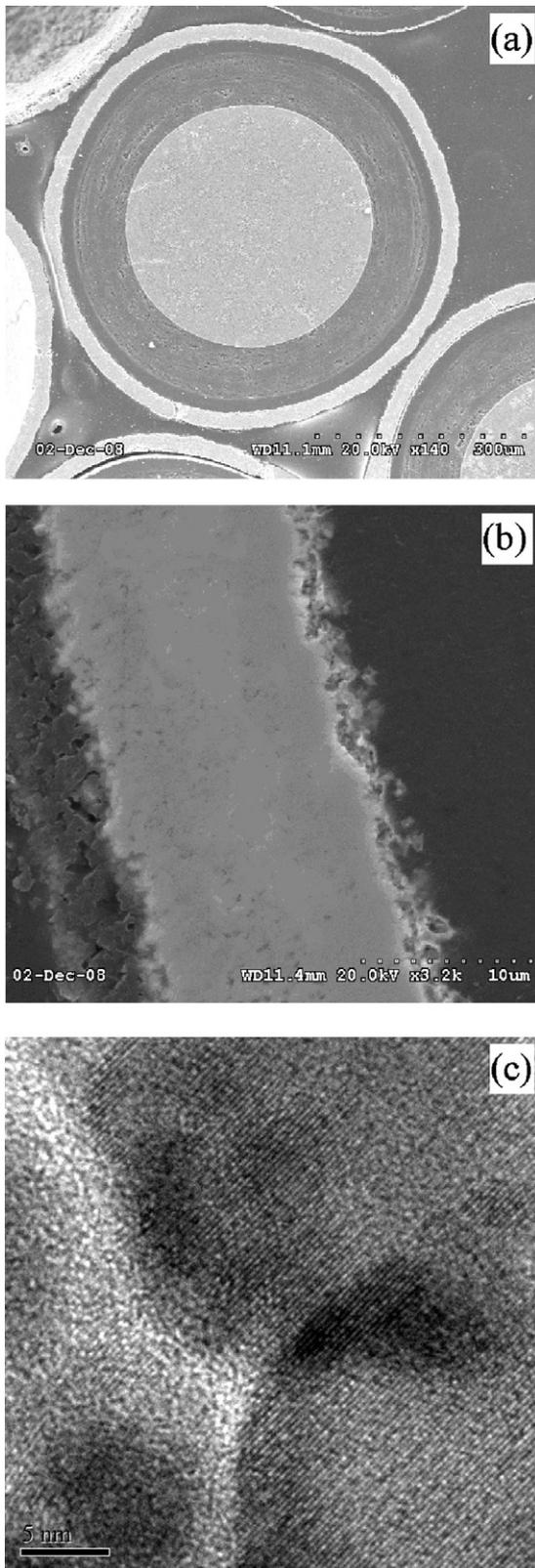


Fig. 4. (a) Section photograph of a ZrC-coated particle with ZrO<sub>2</sub> kernel and two pyrocarbon layers, (b) close up image of ZrC layer, (c) TEM image of ZrC.

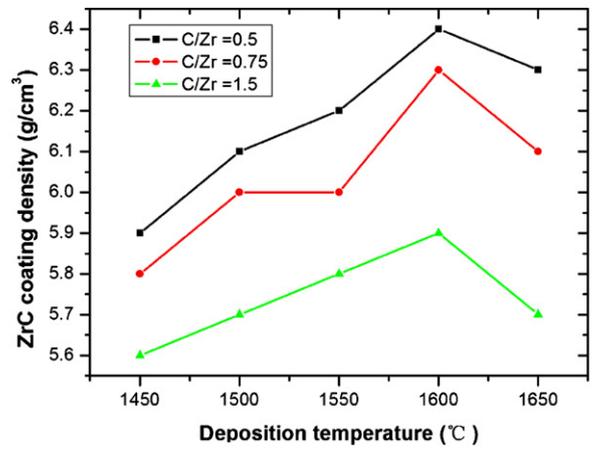


Fig. 5. ZrC layer density increases with deposition temperature (C/Zr is atomic ratio in gas).

ZrC coating layer has great role in the irradiation performance. Ideal ZrC coating has a 1:1 atomic ratio of C/Zr, but it determined by C and Zr source in deposition gas. The first C/Zr ratio in gas comes from flow ratio of C<sub>3</sub>H<sub>6</sub>/ZrCl<sub>4</sub> which goes into fluidized bed. Consider gas (C<sub>3</sub>H<sub>6</sub> and ZrCl<sub>4</sub>) pyrolysis and deposition efficiency, C/Zr ratio of gas is higher than 1:1 ratio. Experimental results give the same conclusion, as showed in Fig. 6, when C/Zr ratio is more than 1.0, the carbon XRD diffractive peak appears, it means that excessive C in gas deposited in coating layer and lead to decrease in density, as showed in Fig. 5. Correspondingly, more porous appear in the fracture surface microstructure of the coating layer. But C/Zr ratio's

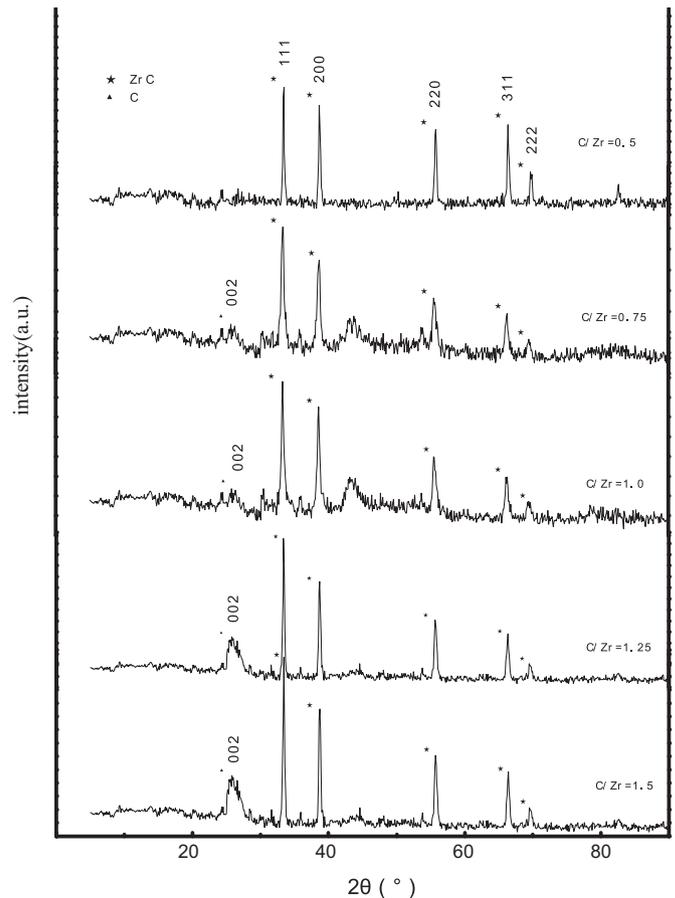


Fig. 6. XRD of ZrC coating deposited with different C/Zr ratio in gas.

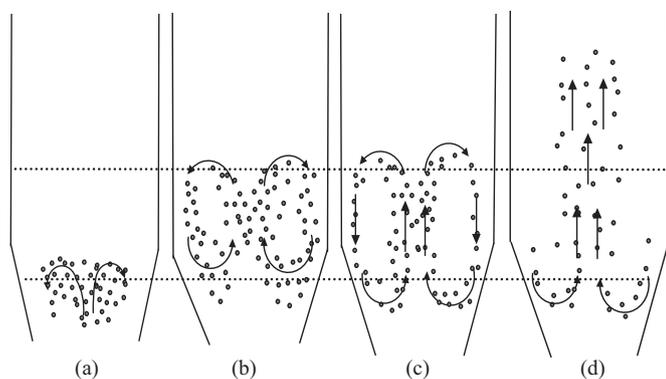


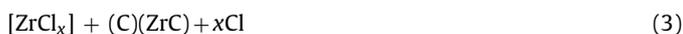
Fig. 7. The particles fluidization with various Ar flows (the area between two dash lines is the central temperature zone).

effect discussed here is different in various deposition conditions, for temperature and gas total flow in fluidized bed have complex effect on deposition process. In addition, the signals around  $35^\circ$  in XRD suggest that  $ZrO_2$  appears in coated layer, especially in the 0.75 and 1.0 C/Zr ratio. This oxide may be due to the impurity of  $ZrCl_4$ .  $ZrCl_4$  powder is easy to absorb water in air when it is loaded into evaporation vessel. It can be avoided by a glove box.

As mentioned above, deposition temperature and reaction gas ( $C_3H_6$  and  $ZrCl_4$  vapor) have great effect on ZrC coating layer properties and microstructure, but all effects are based on the atmosphere provided by Ar flow and pressure. In deposition gas composition, argon (Ar) is carrier gas for fluidization and  $ZrCl_4$  vapor. For a given particles batch in a fixed fluidized tube, Ar flow and pressure are designed to keep a good fluidization in the temperature zone, so the particles get a fluid density, which decides reaction probability between particles and radicals. Ar flow rate will affect gas residence time and gas maturation of intermediate molecules. Furthermore a good fluidization will ensure that substrate particles do not remain stationary, which is the most important task that should be avoided in a fluidized bed, where temperature gradients, residence times, etc. change with distance from the nozzle. Ar gas flow effect in fluidized bed CVD deposition is illustrated in Fig. 7 (Xu Xiaoping, 1999), first is to keep particles in a fluidization state, second is to give a proper particles fluid density, and third is to keep the particles in the central temperature zone. In Fig. 7(a and d), the fluidization is not acceptable; (b and c) are proper fluidization for deposition, but (c) has a low fluid particles density. Unfortunately, most of the hot fluidization can only be observed by eyes on the top of the fluidized bed, (a and d) states are easy to be found out, but (b and c) states are not easy to distinguish. So Ar gas flow and pressure in a fixed fluidized bed are relatively stable.

#### 2.4. Mechanism discussion in fluidized bed CVD deposition

If fluidization is accommodable,  $C_3H_6$  and  $ZrCl_4$  vapor provide enough C and Zr source, the CVD deposition process is controlled by chemical equilibrium and mass balance, which are dependent on deposition temperature and  $H_2$  gas flow. This is a mixture chemical reaction process, the key reactions are described as following:



In the CVD deposition, two contrary processes of pyrolysis (Eqs. (1) and (2)) and synthesis (Eqs. (3) and (4)) simultaneously occur,

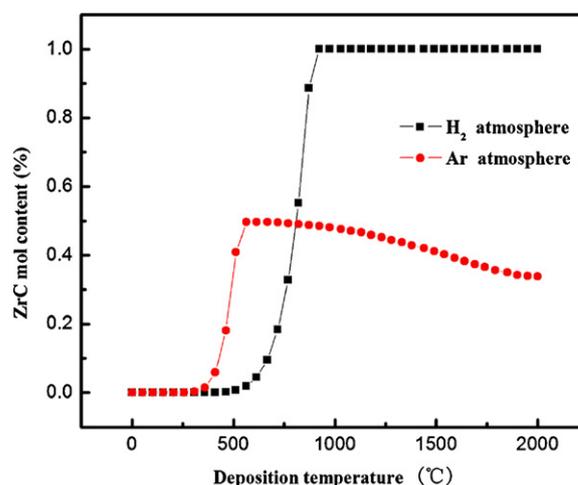


Fig. 8. Correlation between calculated ZrC mol content and deposition temperature in  $H_2$  and Ar atmosphere.

two processes reach an equilibrium at certain temperature. Several factors support the equilibrium, such as reaction reversibility, competing reactions and stability of the intermediate products; temperature provides a power for the reactions and also affects reaction direction. High temperature accelerates pyrolysis of  $C_3H_6$  and  $ZrCl_4$ , but too high temperature reduces the density of ZrC coated layer, because it changes direction of reaction. Results in Fig. 5 show that coated layer density decreases at deposition temperature  $1650^\circ C$ .

$H_2$  gas is a reducer in pyrolysis process of  $C_3H_6$  and  $ZrCl_4$ , it also affects the CVD chemical equilibrium in reactions of Eqs. (1)–(4), and decides stability of various intermediate products and final product. Theoretical calculation results exhibit the great role of  $H_2$  in CVD deposition. Fig. 8 is a calculation result of ZrC coating layer CVD deposition thermodynamic, in Ar atmosphere, the maximum ZrC mol content is 50%, but in  $H_2$  atmosphere, it reaches 100% when temperature is above  $800^\circ C$ .

### 3. Summary

ZrC coating is deposited by fluidized bed CVD method with a mixture of  $ZrCl_4$  power feeder and evaporation supply. Tested results of  $ZrCl_4$  vapor pressure evaporation rate are high enough for CVD deposition rate in fluidized bed. In this apparatus, low C/Zr atomic ratio in gas and high deposition temperature increase the ZrC coating density. Ar flow and pressure are adjusted to get a good fluidization which keeps most of the particles in a uniformity fluid density and in the central temperature zone.  $H_2$  gas has a great role in the CVD deposition chemical equilibrium.

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