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Experimental study on the generation of carbonaceous dust formed by chemical vapor deposition in HTGR

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ABSTRACT

Carbonaceous dust can bring some potential threats to the safe operation of the high temperature gas-cooled reactor. Predictive models based on physical generation mechanism have produced errors in regards of actual observations. Thus, the chemical generation mechanism is worth investigating. This paper mainly analyzes the formation of carbonaceous dust by chemical vapor deposition with carbon monoxide and hydrogen mixture as feed gas. The adopted substrate is made of Inconel 617 alloy. The effect of hydrogen content and reaction temperature on the generation of carbonaceous dust have been investigated. The morphology and microstructure of the deposited carbonaceous dust have been characterized by scanning electron microscope, energy dispersive spectrometer, and Raman spectrum. The experimental results show that the production of the carbonaceous dust is almost in parabolic relationship with H_2 flow rate, while for the influence of reaction temperature, the result is much closer to exponential relationship. In addition, two kinds of carbonaceous dust particles, larger agglomerate particles and small isolated particles, have been observed.

1. Introduction

The high temperature gas-cooled reactor (HTGR), a promising candidate for the next generation of nuclear power plants, has gained considerable attentions due to its intrinsic safety, high thermal efficiency, and resistance to proliferation. In HTGR, graphite has been widely adopted, serving as moderator, reflector and structural material (Baker, 1971; Singh et al., 2017; Xing et al., 2014). In 10 MW high temperature gas-cooled reactor (HTR-10) which is designed by Tsinghua University, nearly 60 tons of graphite and 27,000 fuel elements have been used (Luo et al., 2008). In addition, for the high temperature gas-cooled pebble-bed modular reactor (HTR-PM) which is developed on the basis of HTR-10, there are about 420,000 fuel elements adopted in each module of HTR-PM (Yu and Yu, 2010).

During the lifetime of HTGR, massive amounts of carbonaceous dust can be generated, which will bring some potential threats. The dust can combine with fission products, such as cesium, strontium, iodine and tritium (Kissane, 2009), and deposit on the surface of the primary circuit, affecting heat transfer and complicating the maintenance (Lind et al., 2010). The radioactive dust may even eject into the environment during depressurization accident (Moormann, 2008). In addition, for direct cycle helium gas turbine, these carbonaceous particles can collide with the blades, decreasing their service life (Cogliati et al, 2011). Therefore, the generation mechanism of the carbonaceous dust should be carefully studied.

Past research has mainly focused on the physical generation mechanism of the carbonaceous dust. Boddu et al. (2011) analyzed the morphology of carbon particles produced by spark generator and simulated the particle deposition by computational fluid dynamics. This group also experimentally characterized the charge and size distributions by tandem differential mobility analyzer (Simones et al., 2011). Luo et al. (2004, 2005a, 2005b) performed experiments to analyze the effects of temperature, external force and gas environment on the wear behavior of nuclear grade graphite IG-11. Based on the wear experiments, they roughly estimated that the dust generation in HTR-10 under normal operating condition is 2.74 kg per annum (Luo et al., 2005c). They also further estimated dust production both by energy balance method and by discrete element method (Luo et al., 2017). However, during our recent maintenance for HTR-10, we have found that the actual dust production is much more than estimated. In addition, Cogliati and Ougouag (2008) also built up a model to assess the dust production in AVR. A large discrepancy between the predicted production and actual observation (Bäumer et al., 1990; Moormann, 2008) was also discovered. Thus, in order to explain the observed errors, other generation mechanisms need to be further investigated.

The primary circuit of HTGR usually contains some low-level

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Table 1
Maximum tolerated values of the gaseous impurities in the primary helium coolant of HTR-PM (Yu and Yu, 2010).

Impurities	Maximum tolerated value ($cm^3 \cdot m^{-3}$)
H_2	30
H_2O	2
CO	30
CO_2	6
CH_4	5
O_2	0.2
N_2	2

gaseous impurities, such as carbon monoxide (CO), carbon dioxide (CO_2), methane (CH_4), hydrogen (H_2), water vapor (H_2O), nitrogen (N_2), oxygen (O_2). Table 1 presents the maximum tolerated values of the gaseous impurities in the primary helium coolant of HTR-PM (Yu and Yu, 2010).

These gaseous impurities can be derived from refueling, maintenance and chemical reactions (Kissane, 2009). The following presents the possible reactions that can happen in the reactor core at high temperatures (Kelly et al., 2000).

$1/2O_2 + C = CO$

$O_2 + C = CO_2$

$1/2O_2 + CO = CO_2$

$C + CO_2 = 2CO$

$C + H_2O = CO + H_2$

$C + 2H_2O = CO_2 + 2H_2$

$C + 2H_2 = CH_4$

$CO + H_2O = CO_2 + H_2$

Considering the reversibility of the chemical reactions, these gaseous carbon-containing compounds which are generated in the core can serve as carbon sources to produce solid carbon through reverse reactions, the process of which can be regarded as chemical vapor deposition (CVD). Besides, some researchers also mentioned the chemical generation mechanism of the carbonaceous dust in their publications. Nieder (1990) once proposed that the carbonaceous dust could be generated by chemical reactions of CO disproportionation and CO hydrogenation. Hanson (2008) also put forward that CO disproportionation could cause small quantities of carbonaceous dust. In addition, Idaho National Laboratory researchers once held meeting to evaluate HTGR dust safety issues; they mentioned that to explain the large discrepancy between the experimental data and predictive model, further research on chemical reactions need to be added in their future plan (Humrickhouse, 2011). Therefore, it is necessary to study the chemical generation mechanism of the carbonaceous dust.

This paper mainly analyzes the deposition of carbonaceous dust by CVD on Inconel 617 alloy. The effects of H_2 content and reaction temperature on carbonaceous dust production are discussed. The morphology and structure of the deposited dust was characterized by scanning electron microscope (SEM), energy dispersive spectrometer (EDS) and Raman spectrum. In addition, a micro balance was adopted to measure the production of the obtained carbonaceous dust. This paper is organized as follows. The CVD system and experimental procedure are demonstrated in Section 2. The experimental results are presented in Section 3. Finally, the conclusions of this paper are drawn in Section 4.

2. Experimental setup

The experimental CVD system is shown in Fig. 1. The CVD chamber

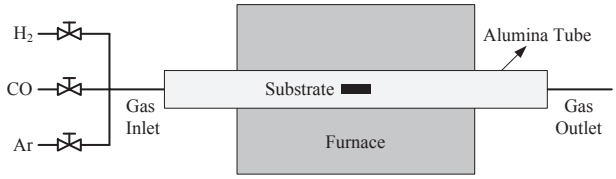

Fig. 1. The schematic setup of the experimental CVD system.

is made of an alumina tube with an inner diameter of 80 mm, for which the upper limit of temperature is 1600 °C. During our experiments, the reaction pressure was kept at 1 atm. Because of our experimental platform, the effects of CO and H_2, whose maximum tolerated values are much higher than other gaseous impurities, have been mainly analyzed. Additionally, argon (Ar) was employed as the carrier gas. The purities for CO, H_2 and Ar are 99.9%, 99.99% and 99.99%, respectively. As for the substrates, they were manufactured from bulk material into 1 mm × 50 mm × 50 mm slices, and then they were mechanically polished. The substrates are made of Inconel 617 alloy, which is a typical nickel-based alloy. There are four types of alloys that have been considered for application in heat exchangers and core internals for the next generation of nuclear power plants, namely Inconel 617, Haynes 230, Incoloy 800H and Hastelloy XR, among which Inconel 617 has been viewed as the most probable candidate because of its technical maturity, high temperature mechanical properties, experience base and so on (Wright, 2008). The chemical compositions of the studied Inconel 617 alloy are listed in Table 2.

The experiments were conducted by the following procedures. To remove the impurities attached to the substrates, before the experiments, the substrates were cleaned by alcohol in an ultrasonic bath for 10 min, and then they were dried in a vacuum drying oven at 60 °C for 10 min. After the pretreatments, the blank substrates were put into the center of the alumina tube and the vacuum pump was turned on to remove the residual air in the tube. Once the tube was pumped to a pressure lower than 1000 Pa, 100 $ml \cdot min^{-1}$ Ar was introduced to recover the pressure to 1 atm. Then, the heating system was turned on to heat the furnace. Fig. 2a is the recorded time-varying temperature of the furnace center. In our experiments, five reaction temperatures were analyzed, namely 600 °C, 700 °C, 800 °C, 900 °C and 1000 °C, which covers the coolant outlet temperatures. In all experiments discussed here, the heating-up time was settled at 120 min and then the temperature was kept at constant value for 60 min, after which the heating system was turned off and the temperature of the furnace cooled down gradually. Fig. 2b illustrates the different flow rates of the adopted gases at the corresponding time. At first, only 100 $ml \cdot min^{-1}$ Ar was injected. Once the furnace reaches the required temperatures, the supply of Ar was cut off. Meanwhile, 100 $ml \cdot min^{-1}$ CO was introduced and the flow rate of H_2 was adjusted to a certain value immediately. After reacting for 60 min, only 100 $ml \cdot min^{-1}$ Ar was introduced to cool down the CVD system.

3. Results and discussion

Considering the ratio between H_2 content and CO content fluctuants during the actual operation of HTGR, it is necessary to analyze the influence of H_2 content. Fig. 3 presents the influence of H_2 flow rate on the generation of the deposited carbonaceous dust over each substrate at 800 °C reaction temperature. Each experiment was performed three times, and the means and standard deviations as error bars have been graphed. It can be found that with the increase of H_2 flow rate, the production of the deposited carbonaceous dust rises to a certain value and then declines, the relationship between which is almost parabolic. The maximum production appears at 25 $ml \cdot min^{-1}$ for the adopted H_2 flow rate and the flow rate ratio between H_2 and CO is 1/4. To understand the influence of H_2, two chemical reactions have been analyzed (Bladh et al, 2000; Zheng et al., 2002).