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SYNTHESIS AND PROPERTIES OF ZIRCONIUM CARBIDE FILM ON GRAPHITE

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Abstract

In this study, synthesis and properties of zirconium carbide on graphite will be introduced. CVD temperature and H_2 flow affect properties of ZrC film. The increased temperature and increased size of crystal ZrC reduce flatness of the surface; contrarily, the increased flow of H_2 and decreased size of crystal flatten the surface of porous film. The obtained results showed that CVD condition is suitable for producing uniform, consistent and flat ZrC film: temperature 1200 °C; H_2 flow at 20 ml/min; flows of Ar, gas at 30, 80 ml/min, respectively; $ZrCl_4$ 8 g/time, CVD time 1 hour. Phase components of ZrC film mainly consist of two principal phases ZrC and carbon. Film thickness ranges from 10.5-15.5 µm; film coating is uniform, non-crack, and highly compact and the film's medium hardness is 1943 kG/mm^2.

Keywords: Zirconium carbide, film, graphite, CVD.

1. INTRODUCTION

Carbide film in general and zirconium carbide film in particular were studied in the early 1970s. However, just recently, they were researched and developed. Owing to preeminent properties of ZrC film such as: chemical resistance, heat conductivity, good thermal shock resistance, high melting point (3450 °C) [1-5], it is used in some hi-tech areas such as: coating layer of radioactive element cylinder, components used in aerospace industry and coating of fire line shell in all the long-range missiles [6-13]. Originating from actual demands and needs, we have studied on synthesis and properties of zirconium carbide film on graphite.

2. EXPERIMENTAL

2.1. Produce the ZrC film

ZrC film is synchronized by CVD method (chemical vapor deposition) [14-16] on basis of $ZrCl_4$ precursor of Merck, gas of Malaysia, H_2, Ar of Singapore on graphite. Synthesis process is conducted as follows (figure 1): sample of graphite substrate, after fed into the reactor cell, has Ar gas blown to clear up steam and oxygen, and then heated at 10 °C/min. Up to required temperature, the heat will be maintained for 15 minutes so that the sample and CVD region are thermally uniform and concurrently $ZrCl_4$ container is heated to 300-350 °C and H_2, gas valves are opened. At that time, in the reactor cell, reactions below may occur:

$$\text{Gas} \xrightarrow{T^oC} CH_4 + C_2H_4$$

$$CH_4 \xrightarrow{T^0C} C\ (CH_3, C_2H_2...) + H_2$$

$$ZrCl_4 + H_2 \xrightarrow{T^0C} Zr\ (ZrCl_3, ZrCl_2...) + HCl$$

$$Zr(ZrCl_3, ZrCl_2...) + C\ (CH_3, C_2H_2...) \rightarrow ZrC + HCl$$

2.2. Survey on properties of ZrC film

Surface structure of ZrC film is studied by imaging with scanning electron microscope (JEOL 6610, Japan). Phase component of the film are identified by X-ray diffraction on SIEMENS D 5005 device, source of emission Cu Kα, crystal monochromatic filter lens, Al_2O_3 buffer, rotary speed 3.03°/0.5s. Hardness of the film is calculated by measuring Vickers hardness on microscopic hard measuring device MHT-10-microscope AXIOVERT 25CA (Germany).

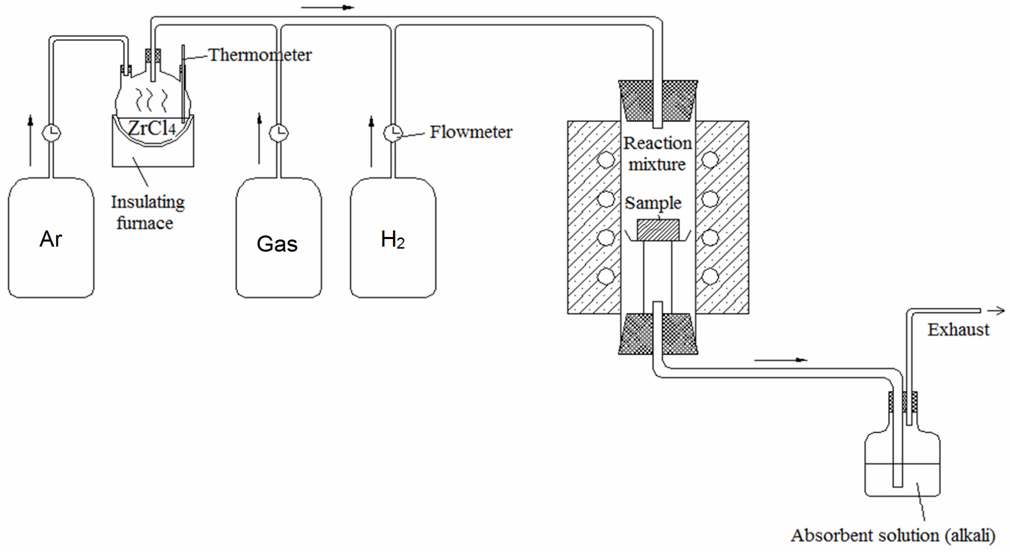

Figure 1: Schematic of ZrC film synthesis

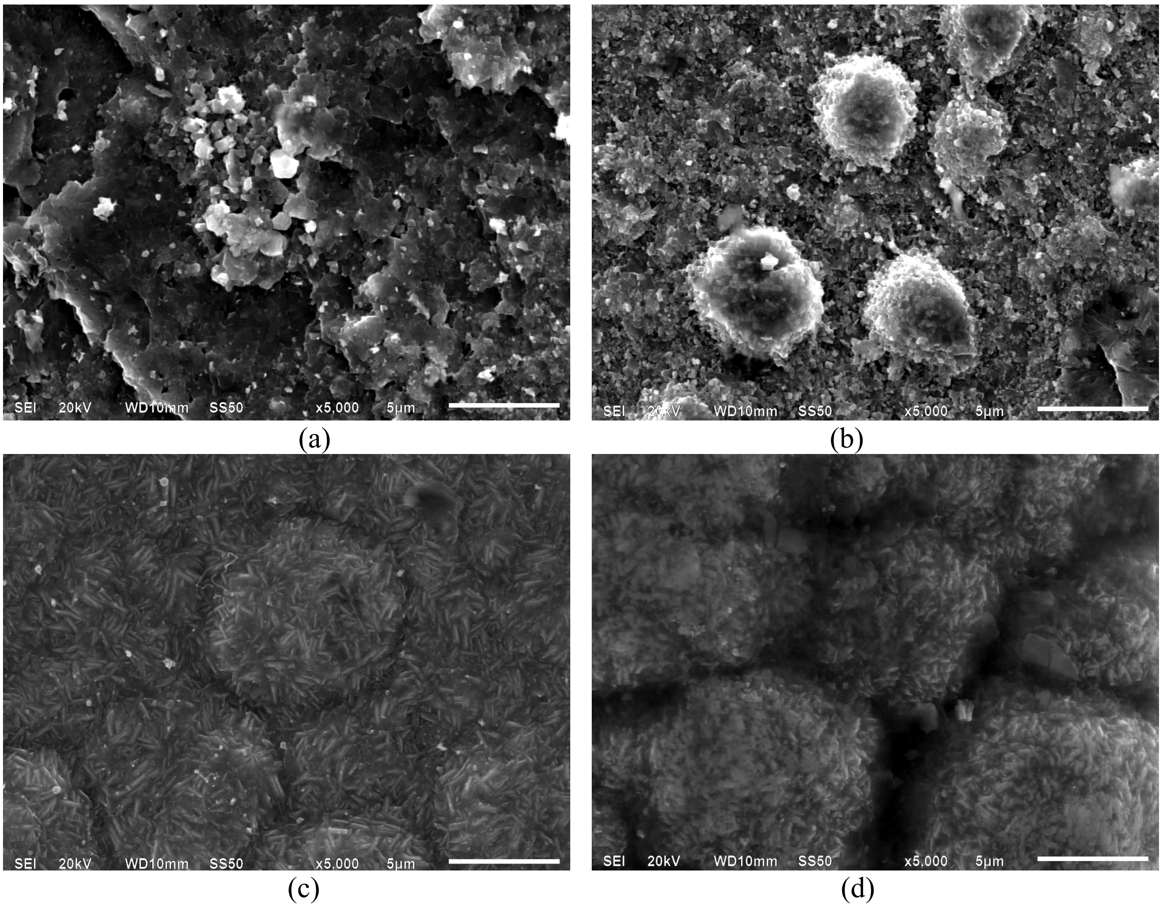

Figure 2: SEM image of ZrC film coated at different temperatures: (a) 1000 °C, (b) 1100 °C, (c) 1200 °C and (d) 1300 °C

3. RESULTS AND DISCUSSION

3.1. Influence of CVD temperature and flow of H_2 on formation of ZrC film

Study on the thermal influence is conducted by changing CVD temperature 1000; 1100; 1200; 1300 °C; unchanging conditions: flows of H_2, Ar, gas at 20; 30; 80 ml/min respectively, $ZrCl_4$ 8 g/time, CVD time 1 hour.

Figure 2 is the SEM images of ZrC film at different temperatures.

The image displays that at 1000 ^oC, tiny crystals appear on graphite surface but not uniform because some positions have not been covered. When CVD temperature reached 1100 ^oC, the coverage was raised significantly. Crystals on the surface tend to develop bigger and bigger; size of the largest crystal is about 5 μm. From those crystals, we will develop to the compact and consistent crystals on the base surface [14, 15]. Temperature is continued to be increased to 1200 ^oC, on the surface there are uniform, flat, compact crystals in average size of 5-7 μm. When it was raised to 1300 ^oC, size of the crystals on the surface accordingly rises to 8-14 μm. However, their compactness and uniform declined, which resulted in reduction of compactness of the surface. Therefore, it is better to carry out CVD at 1200 ^oC in order to ensure uniform of film structure.

Influence of H_2 flow is studied by changing the H_2 flows at 0; 20; 40 ml/min in turn, unchanging the conditions: Ar, gas flows at 30; 80 ml/min respectively, temperature 1200 ^oC, $ZrCl_4$ 8 g, CVD time 1 hour.

Figure 3 illustrates SEM images of ZrC film samples that react at different H_2 flows.

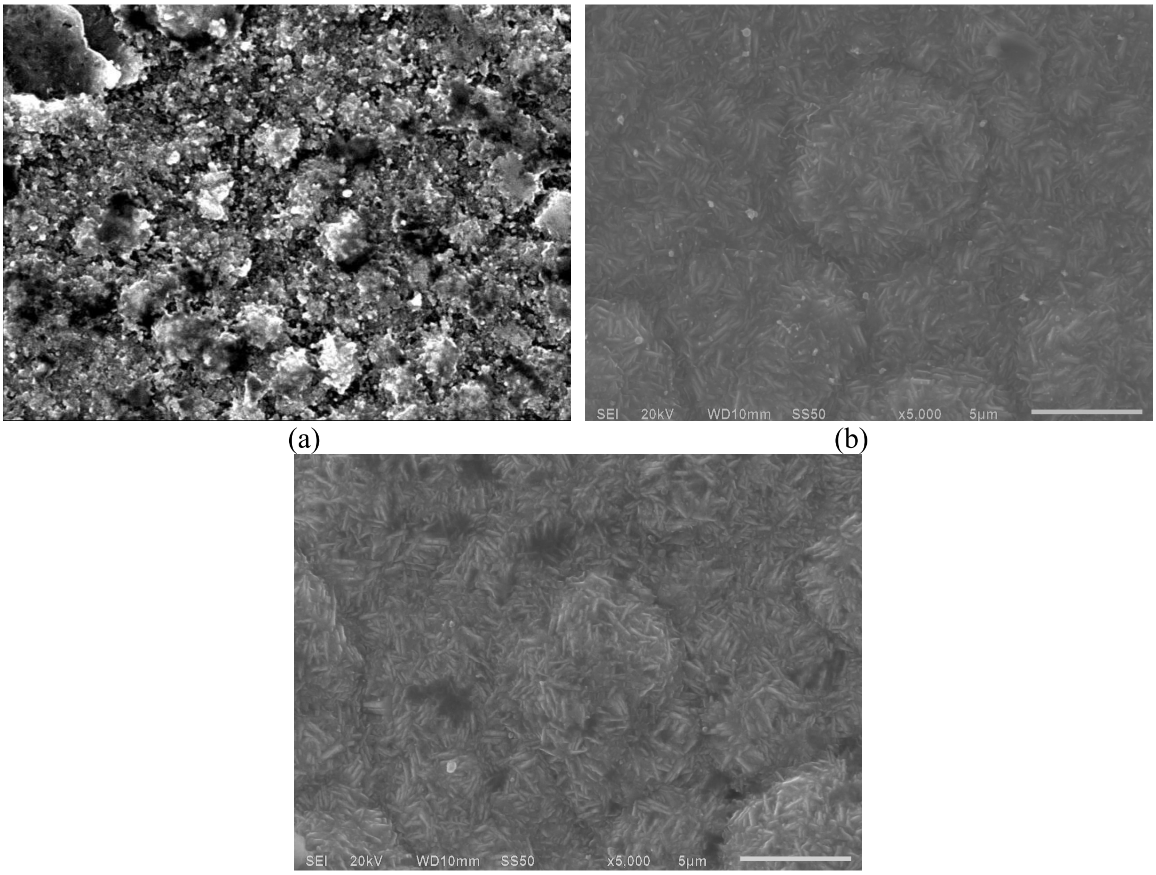

Figure 3: SEM image of ZrC film at H_2 flows 0; 20; 40 ml/min corresponding to a; b; c

The image shows that on the absence of H_2, there is non-uniform coating layer on the surface because some positions are not covered. This is suitable with [9], applying the dynamic thermal computing program SOLGASMIX-PV; without H_2, ZrC film formation process becomes poor. When H_2 flow was raised to 20 ml/min, morphology of surface changed obviously. On the surface, there are uniform, flat, high compact crystals in average size of 5-7 μm. When H_2 flow was raised to 40 ml/min, the surface changed from big crystal clusters into smaller crystal clusters. The image also shows that micropores appear on the surface. Such results demonstrate that H_2 has considerable influence on capability and process of ZrC film formation because it is not only a diluting agent like Ar but also an agent directly joining in reaction process [15].

3.2. Study some properties of ZrC film

Post-CVD sample in conditions: temperature 1200 ^oC, H_2 flow at 20 ml/min, Ar, gas flows at 30; 80 ml/min respectively, $ZrCl_4$ 8 g, CVD time 1 hour, had its phase components, thickness and hardness of the film studied.

3.2.1. Study on phase components of the film

X-ray diffraction diagram of ZrC film is shown in figure 4.

Results show that ZrC film is composed of two main phases, ZrC phase in the pictures corresponding to d = 2.7067; 2.3451; 1.6570; 1.4134 and 1.3541 Å and carbon phase in the pictures corresponding to d = 3.371; 2.1321 Å. Moreover, ZrO_2 also appear at weaker density in the pictures corresponding to d = 3.164; 2.8403 Å. These results demonstrate that the film on graphite surface is mainly ZrC.

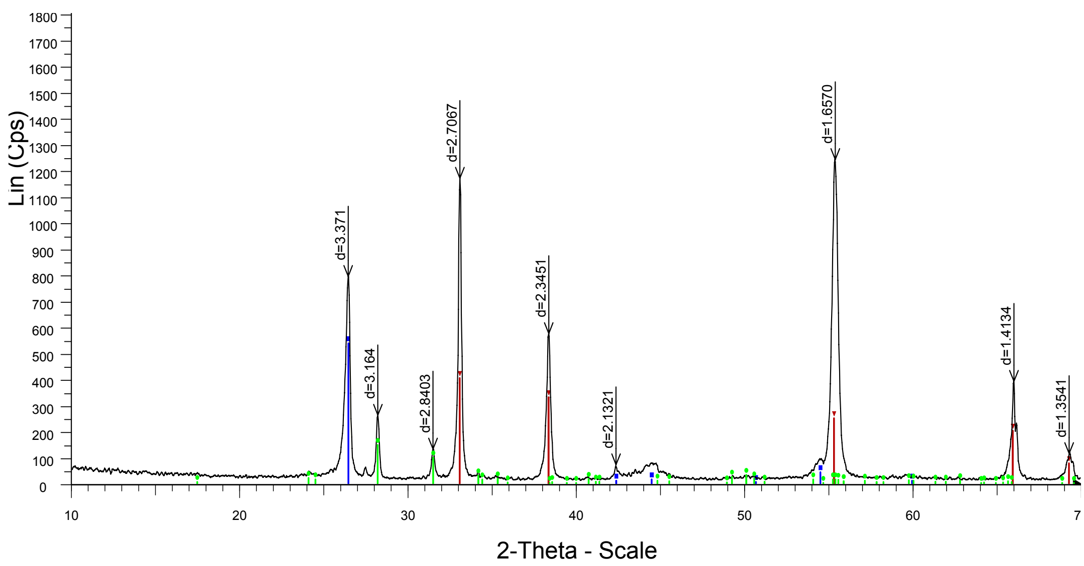

Figure 4: X-ray diffraction diagram of ZrC film

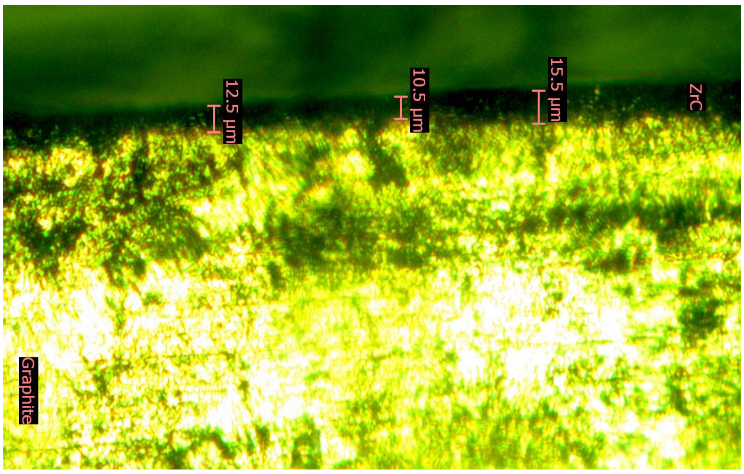

Figure 5: Image of thickness of ZrC film

3.2.2. Study on thickness of the film

Figure 5 represents thickness of the film identified by metallographic method

The image show that bright and soft part is graphite and the dark range along the graphite surface is ZrC film. Thickness of ZrC film is about 10.5-15.5 μm; the coating layer is relatively uniform, non-crack and good compact. Boundary between ZrC film and graphite has no space and coating layer peeling.

2.3. Study on hardness of the film

The samples, after being tested the thickness, will be measure microscopic hardness by method of Vickers hardness with pyramidal point fixed on the optical microscope. The point is directly guided to the coating layer in parallel with surface of base sample. Table 1 represents the measuring results of microscopic hardness of the ZrC film.

Table 1: Measuring results of Vickers hardness

No. Measurement	Microscopic hardness, kG/mm^2
	ZrC film
1	1916
2	1954
3	1959
Average	1943

Those results display difference of three measurements, of which the measurement 1 is noticeable because its hardness value is much lower than the measurements 2 and 3. The reason may be compactness of the film in position of measurement 1 is worse than the measurements 2 and 3. Average hardness is 1943 kG/mm^2 lower than 2550 kG/mm^2 of standard sample ZrC [1]. As a result, further study should be conducted on influence of film formation on hardness of ZrC film.

4. CONCLUSIONS

The research on synthesis and properties of ZrC film on graphite shows that CVD conditions that are suitable for forming the uniform, compact and flat ZrC film are: temperature 1200 ^oC; H_2 flow at 20 ml/min; flows of Ar, gas at respective 30; 80 ml/min; $ZrCl_4$ 8 g, CVD time 1 hour. CVD temperature and H_2 flow affect properties of the film. Raise in temperature that increases size of ZrC crystal reduce the surface flatness. If the flow goes up, the film surface will become softer.

The phase components of ZrC film consist of two main phases: ZrC phase and carbon phase. The film thickness is about 10.5-15.5 μm; the coating layer is uniform, non-crack, high compact and the film hardness is 1943 kG/mm^2 on average.

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