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Preparation of Zirconium Carbide-Zirconium Silicide Composite Powders by Solid Reaction of Zr and SiC Powders

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In the present work, zirconium carbide-zirconium silicide composite powders were prepared by solid reaction using Zr and SiC powders as reactants. Scanning electron microscopy (SEM) and X-ray diffraction (XRD) results showed that, after treatment at 800 ºC, the produced zirconium carbide-zirconium silicide diffusion layer was very thin and mainly consisted of ZrC and $ZrSi_2$. After treatment above 900 ºC, the produced phases were mainly consisted of ZrC and $ZrSi_2$, plus less ZrSi.

Keywords: zrconium carbide, zirconium silicide, composite powder, solid reaction.

1. INTRODUCTION

ZrC is attracting more and more attention for applications in thermal protection systems for hypersonic flight, atmospheric re-entry and rocket propulsion due to its high melting points (3540 ºC), low densities (6.7 g/cm^3) and excellent wear resistance [1, 2]. However, the application of ZrC ceramics in single phase is quite limited due to their low oxidation resistance [3, 4], besides sintering of ZrC is difficult due to its covalent nature and high melting point.

Research has confirmed that $ZrSi_2$ can significantly lower the onset densification temperature of ZrB_2 ceramics [5]. Addition of $ZrSi_2$ can also improve the oxidation and ablation resistance for ZrB_2-SiC and SiC coating [6, 7]. It also has been demonstrated that ZrC-$ZrSi_2$-SiC coating possesses improved oxidation and thermal shock resistance [8].

Compared with blended powders, composite powders are more favorable to improving densification kinetics during sintering and thus improving the density and mechanical properties of sintered body [9, 10]. Therefore, ZrC-$ZrSi_2$ composite ceramic powders with fine and homogeneous structure is very important to act as precursors of composites. However, reports on the synthesis of ZrC-$ZrSi_2$ composite ceramic powders are lacking.

Earlier works have demonstrated that ZrC-ZrB_2, TiC-TiB-TiB_2 composite ceramic powders can be prepared by solid reaction between powder of Zr or Ti and B_4C [11, 12]. High vacuum heat treatment between 700 to 850 ºC for 30 min, Zr film deposited on SiC substrate reacts and forms ZrC and Zr silicides (Zr_2Si, $ZrSi_2$ and Zr_5Si_3) [13]. The work conducted by Bhanumurthy *et al.*, compacted SiC powder filled in Zr cup and compressed to make sure intimate contact were used to study the diffusion of them. It has confirmed that heat treatment at 1100 to 1300 ºC in argon for 144 h, leads to in-situ solid reaction between Zr and SiC and formation of Zr_5Si_3C, Zr_2Si and ZrC. However, it is also reported experiment using small pieces of Zr and SiC powder were not successful [14]. Therefore, it is necessary to study whether solid reaction can occur between loose powder of Zr and SiC and to confirm the produced products.

In the present work, the solid reaction between Zr and SiC powder mixtures under low pressures and preparation of zirconium carbide-zirconium silicide composite powders by solid reaction of Zr and SiC powders was studied.

2. EXPERIMENTAL PROCEDURE

Zirconium (Zr) powders (ABCRTM, 99.9 % purity, with an average particle size of to 1 – 5 μm) and silicon carbide powders (SiC) (BeiJing TopVendor Science &Technology CO., Ltd, 99.9 %, with an average particle size of about 0.5 μm) are used as initial powders. It has been demonstrated that the produced phases by reactive diffusion between Zr and Si was mainly in $ZrSi_2$ plus less ZrSi [15]. In order to make SiC completely reaction consumed, the molar ratio of Zr to SiC should be slightly smaller than 3:1. The mixture composition with molar ratio of Zr:SiC of 3:1 was used. The powders mixture treated at 800 °C to 1000 °C for different times.

The phase composition was identified by using X-ray diffraction (XRD, BRUKER, D8 ADVANCE A25 X). XRD analysis was operated at 40 kV and 40 mA. Step scans were taken in the range of $2\theta = 30 - 80$ ° with a 0.02-step, 0.1º s^{-1} scan speed and a 2 s exposure. The microstructure of the powders was characterized by scanning electron microscopy (SEM, S-4800, Hitachi) equipped with an Energy Dispersive Spectrometer (EDS).

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3. RESULTS AND DISCUSSION

Fig. 1 shows the XRD patterns of the heat-treated mixture of Zr and SiC powders. Peaks of ZrC and $ZrSi_2$ are detected for all of the treated powder mixtures, which confirming formation of zirconium carbide-zirconium silicide composite powders.

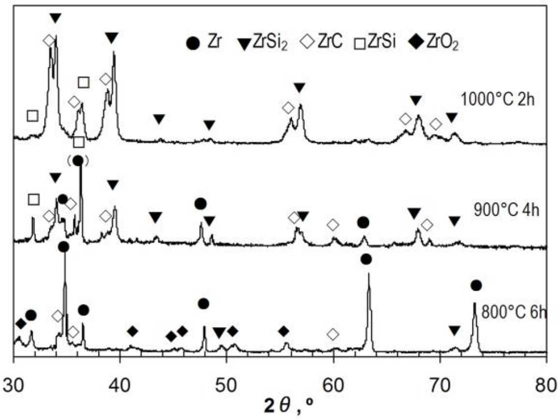
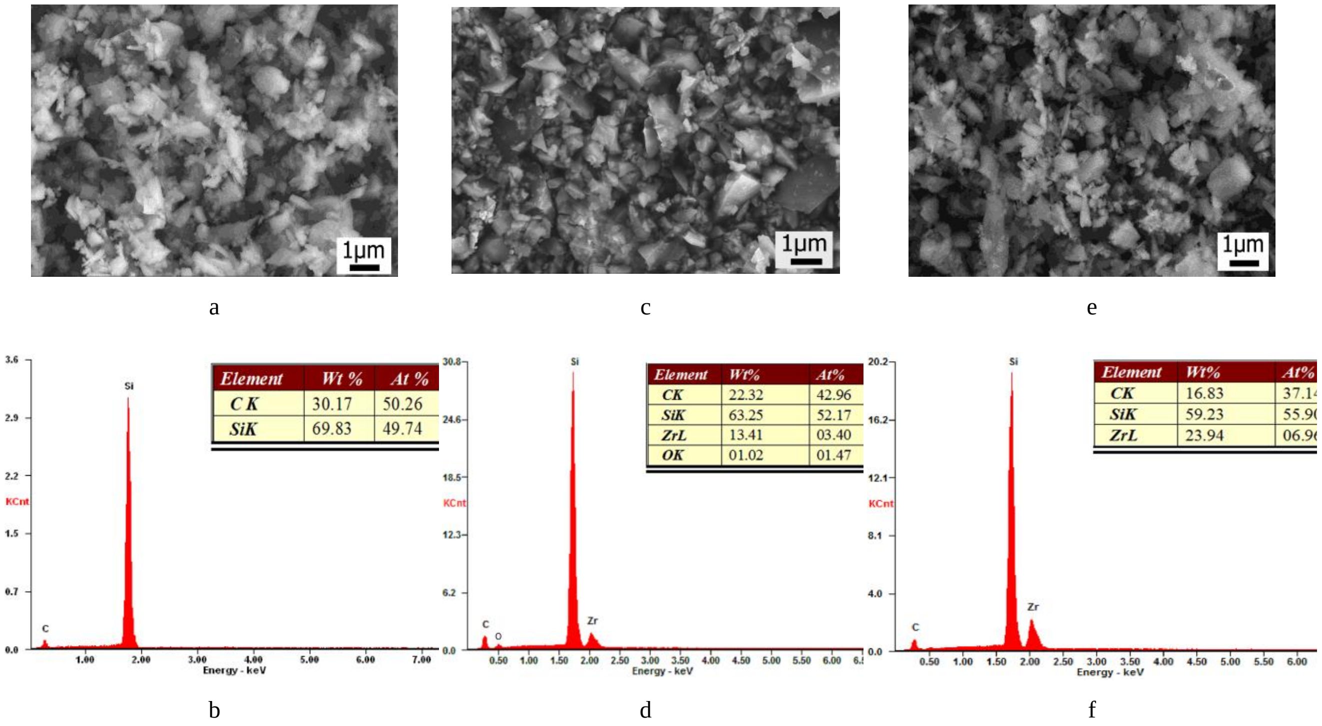


Fig. 1. XRD patterns of the heat-treated mixture of Zr and SiC powders

After treatment at 800 °C, evident peaks corresponding to Zr and very weak peaks corresponding to ZrC and $ZrSi_2$ suggest that the zirconium carbide-zirconium silicide layer is very thin and the reaction is incomplete. It also should be noted that peaks corresponding to ZrO_2 are detected. After treatment at 900 ºC, peaks corresponding to Zr, ZrC, ZrSi and $ZrSi_2$ are detected. However, no peaks of ZrO_2 are detected. After treatment at 1000 ºC, the produced phases are mainly in ZrC and $ZrSi_2$, less ZrSi is detected. Therefore, the above results indicate that increasing the treatment temperatures facilitates preferentially formed ZrO_2 further react and depleted. Moreover, with treatment temperature increasing, it appeared that the intensity of $ZrSi_2$ and ZrC are significantly increased, the same to the intensity of $ZrSi_2$ to that of ZrC. However, the intensity of ZrSi to that of ZrC decreases with treatment temperature increasing. After treatment at 1000 C, the produced phases contain relatively more balanced amounts of $ZrSi_2$ and ZrC. Therefore, treatment at 1000 ºC for 2 h is suitable for obtaining ZrC-$ZrSi_2$ composite powders for the present used powder mixture.

The above results are similar to those observed by E.G. Njoroge et al. [13] In their work, it is confirmed ZrO_2 was detected by XRD at the interface of Zr films deposition on SiC after respectively thermal annealing at 700, 760 and 800 ºC, while it was undetectable after thermal annealing at 850 ºC. It should be noted that, the produced phases between the Zr and SiC in this work are different to those reported by Bhanumurthy et al. [14] In their work, after treatment at 1100 ºC for 144 h, it is confirmed Zr_5Si_3C was also detected by XRD and EPMA. The effective Gibbs energy of formation of the Zr_5Si_3C is considerably less than all the other phases of zirconium carbides and zirconium silicides, therefore it cannot be the initial phases to form [13]. The treatment time the present work (less than 6 h) and that of the work conducted by E.G. Njoroge et al. [13] was much less than that of the work conducted by Bhanumurthy et al., beside the temperature is lower. The condition is not enough to form Zr_5Si_3C and Zr_5Si_3 [13, 16]. Therefore, the formed phases in the present work are ZrC, ZrSi and $ZrSi_2$.

Fig. 2 shows the SEM micrographs (top) and EDS spectra (bottom) of the as-received SiC powders and the treated mixtures.



a c e

Element	Wt %	At %
C K	30.17	50.26
SiK	69.83	49.74

Element	Wt%	At%
CK	22.32	42.96
SiK	63.25	52.17
ZrL	13.41	03.40
OK	01.02	01.47

Element	Wt%	At%
CK	16.83	37.1
SiK	59.23	55.9
ZrL	23.94	06.9

b d f

Fig. 2. SEM micrographs (top) and EDS spectra (bottom) of the: a, b – as-received SiC powders; c, d – the treated mixture: at 800 ºC for 6 h; e, f – at 1000 ºC for 2

From the EDS results of 800 ºC treated mixture, the detected atomic percent of C, Si, Zr and O is respectively 42.96, 52.17, 3.40 and 1.47, which also suggests the formed diffusion layer is very thin. After treatment at 1000 ºC for 2 h, the detected atomic percent of C, Si and Zr is respectively 37.14, 55.9 and 6.96, which was relatively more balanced than that of treated at other temperatures. Therefore, treatment at 1000 ºC for 2 h is suitable for preparing $ZrC-ZrSi_2$ composite powders using the present powders mixture.

As the powders mixture is sealed in the air, adsorption of oxygen is inevitable for the fine powders. Since Zr is more prone to oxidation than SiC [13, 17] and the adsorbed oxygen is very limited, the possible oxidation product is ZrO_2. On the other hand, ZrO_2 might potentially further depleted due to reaction with SiC and Zr [14]. Possible reactions during the treatment are listed as follows:

$$ZrO_2 + 3SiC + 3Zr \rightarrow 3ZrSi + ZrC + 2CO; \quad (1)$$

$$ZrO_2 + 4SiC + 3Zr \rightarrow 2ZrSi_2 + 2ZrC + 2CO; \quad (2)$$

$$ZrO_2 + 2SiC + Zr \rightarrow 2ZrSi + 2CO; \quad (3)$$

$$ZrO_2 + 2SiC \rightarrow ZrSi_2 + 2CO; \quad (4)$$

$$3Zr + 2SiC \rightarrow ZrSi_2 + 2ZrC; \quad (5)$$

$$2Zr + SiC \rightarrow ZrSi + ZrC; \quad (6)$$

$$3ZrSi + SiC \rightarrow 2ZrSi_2 + ZrC. \quad (7)$$

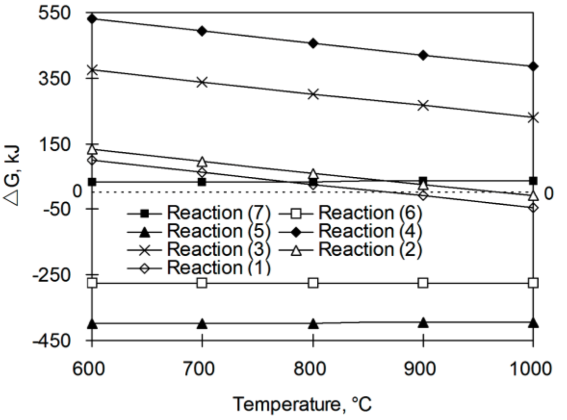


Fig. 3. Variation of Gibbs free energy of the possible reactions with temperatures

Fig. 3 shows variation of the Gibbs free energies (ΔG) of the above reactions as a function of temperatures. It can be seen that over the calculated temperature ranges, Eq. 3, Eq. 4 and Eq. 7 are thermodynamically unfavorable ($\Delta G > 0$), while Eq. 5 and Eq. 6 are thermodynamically favorable ($\Delta G < 0$). It is supposed that Eq. 5 and Eq. 6 is coinstantaneous, $ZrSi_2$, ZrSi and ZrC can simultaneously formed, though the Gibbs free energies (ΔG) of Eq. 5 are lower. The Gibbs free energies (ΔG) of Eq. 2 are positive, except at 1000 ºC. The Gibbs free energies (ΔG) of Eq. 1 are negative above 850 ºC, while positive below 850 ºC. Therefore, the formed ZrO_2 might further reaction to form ZrSi and ZrC above 900 ºC, and thus no peaks of ZrO_2 are detected by XRD for those after treatment above 900 ºC. And the formed products and their contents proportion vary with the proceeding temperatures.

4. CONCLUSIONS

Zirconium carbide-zirconium silicide composite powders can be prepared by solid reaction using Zr and SiC powders. The phase composition and their contents proportion of the formed phases vary with the reaction temperatures. After treatment at 800 ºC, the produced zirconium carbide-zirconium silicide diffusion layer is very thin and mainly consists of ZrC and $ZrSi_2$. After treatment above 900 ºC, the produced phases are mainly consisted of ZrC and $ZrSi_2$, plus small amount of ZrSi. Thermodynamics analysis and experimental results indicate powders mixture with the molar ratio of Zr to Si of 3:1 and treatment at 1000 ºC for 2 h are suitable to make the Zr and SiC completely reacted to form $ZrC-ZrSi_2$ composite powders.

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