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In-situ fabrication of ZrB₂-ZrC-SiCnws hybrid nanopowders with tunable morphologies of SiCnws

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Abstracts

SiC nanowires (SiCnws) with different morphologies have great potential for the reinforcement of ceramic materials. But it is a big challenge in the in-situ synthesis of SiCnws in the ceramic powders which is critical to ensure high reinforcing effects. For the reinforcement of $\text{ZrB}_2\text{-ZrC}$ composites, a simple method is developed to in-situ fabricate SiCnws with various morphologies in nano-sized $\text{ZrB}_2\text{-ZrC}$ powders through pyrolyzing $\text{ZrB}_2\text{-ZrC-SiC}$ gel precursors. The prepared $\text{ZrB}_2\text{-ZrC}$ ceramic powders have mean diameter of about 100 nm with uniformly distributed SiCnw in morphologies of nanocylinder, bead-like, bamboo-shape with tunable nodes, chain-like and hexagonal prisms were prepared by optimizing the preparation process. Moreover, the SiCnws were in a diameter of ranging from 100 to 400 nm, while the length was controlled from tens to hundreds of microns. The generation of ZrB_2/ZrC can determine the formation of SiCnws with specific morphologies by producing CO gas to affect the local supersaturation of the SiO and CO vapors. The study provides an opportunity for fabricating SiCnw reinforced ceramic materials with enhanced strengthening effect and also overcome its critical fabrication process.

Keywords: SiCnws, Morphologies, In-situ synthesis, $\text{ZrB}_2\text{-ZrC}$, Nanopowder,

1. Introduction

As members of ultra-high-temperature ceramics (UHTCs), $\text{ZrB}_2\text{-ZrC}$ ceramics have been considered as one of the most excellent materials for high-temperature applications because of their chemical inertness, high thermal and electrical conductivity, and super thermal shock resistance, etc [1-3]. However, their wide applications in harsh environment are still restricted owe to the low oxidation resistance, intrinsic brittleness, and poor sinterability [4-7].

Recently, $\text{ZrB}_2\text{-ZrC}$ ceramic materials with the addition of SiC have demonstrated improved densification behavior, enhanced mechanical properties and excellent oxidation and ablation resistance at high temperatures [8-13], since the incorporated SiC phase could effectively restrain the crystallite growth, promote the sinterability, and form $\text{ZrB}_2\text{-ZrC-SiC}$ composites with higher eutectic temperature and higher hardness [14-16]. Moreover, SiC nanowires (SiCnws) are used extensively as effective reinforcements with a larger aspect ratio, better strength and elasticity, to enhance the flexural strength and the fracture toughness of ceramic materials [17-20].

As the starting materials to prepare bulk ceramics, ultrafine powders with controlled compositions and microstructures have drawn much attention. $\text{ZrB}_2\text{-ZrC}$ ceramic powders with uniformly distributed SiCnws are critical for the fabrication of $\text{ZrB}_2\text{-ZrC-SiC}$ composites. However, it is difficult to disperse SiCnws homogenously into ceramic powders through ball-milling or other mixing approaches, which would affect the mechanical performance of the prepared composites [21]. To solve this problem, in-situ growth of SiCnws in ceramics is believed to be an effective solution [22-25], in which the synchronous growth of the nanowires and ceramic components can be well achieved.

Furthermore, SiCnws with special morphologies have shown great potential for the reinforcement of structural materials. It is reported that SiCnws with necklace and bamboo morphology could offer enhanced strengthening effect compared with common SiCnws, due to the mechanical interlocking with the matrix [26]. Although great efforts have been devoted to the fabrication of SiCnws with different morphologies, including diameter-fluctuated (such as necklace-like and

bamboo-shaped) [27,28], twinned [29], nanodishes or nanorods [30] etc. There is no report concerning the in-situ synthesis of SiCnws with specific morphologies in the ceramic powders. And it is still a great challenge to fabricate $\text{ZrB}_2\text{-ZrC-SiCnws}$ hybrid powders, due to the difficulty in the control of SiCnws growth during the preparation of $\text{ZrB}_2\text{-ZrC-SiC}$ ceramics, especially in a ternary system with sophisticated gas saturation variation.

Moreover, the sinterability of ceramics is determined by the size and distribution of the starting powders. Usually better refinement and uniformity of the particles are desirable for a better sinterability [31,32]. Recent study suggests that an enormous improvements in terms of optical, mechanical and electrical properties can be acquired through reducing the component size towards nanoscale in the composite materials[33,34]. Sol-gel method is a commonly used approach for the preparation of a wide range of nanocomposites, such as oxide powders, and carbides, boride and nitride UHTCs [35,36], due to the advantages of high purity and homogeneity of the ceramic elements at the molecular level, which may also reduce the particle size and the formation temperature of aimed ceramic phases [37-39].

Therefore, in the present work, $\text{ZrB}_2\text{-ZrC-SiC}$ nanocomposite powders with evenly distributed SiCnws of various specific morphologies in large amount were obtained via a simple sol-gel method, i.e. pyrolysis of as-prepared $\text{ZrB}_2\text{-ZrC-SiC}$ gel precursor. The formation mechanism of $\text{ZrB}_2\text{-ZrC-SiCnw}$ and the growth behavior of SiCnws were investigated, together with the pyrolysis process parameters, such as the heat-treatment temperature and holding time as well as the silicon source in feed. The successful preparation of the $\text{ZrB}_2\text{-ZrC-SiCnw}$ powders provides a new opportunity for the preparation of high-performance SiCnws-reinforced ceramic materials with desirable nanostructures.

2. Experimental Section

In our work, the $\text{ZrB}_2\text{-ZrC-SiC}$ sol precursor was obtained by fully mixing zirconium solution, boron-ethanol solution, silicon-ethanol solution and glucose-water solution. And then, the $\text{ZrB}_2\text{-ZrC-SiC}$ sol precursor was dried and used for the

subsequent heat treatment. To be specific, the zirconium solution was prepared by dissolving $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ (0.01 mol) in ethanol (20 mL) and H_2O_2 (2 mL). The boron-ethanol solution was prepared by dissolving H_3BO_3 (0.02 mol) and PEG-600 (0.05 mL) in boiling ethanol (50 mL). A series of silicon-ethanol solutions were obtained by mixing various TEOS content in ethanol (20 mL). While, the glucose-water solution was prepared by dissolving glucose (0.068 mol) in distilled water (10 mL).

In order to produce SiCnws with different microstructures, precursors, heat-treated temperature and holding times were carefully controlled. A lower processing temperature of 1500 °C and a holding time of 2 h as well as improving the content of silicon in the gel precursor, i.e., the silicon/zirconium molar ratio ($n(\text{Si})/n(\text{Zr})$) in the precursor was varied from 6, 8, 10, 12, 14 to 16, were applied in our work. In comparison, the holding time varied from 1 to 4 h, and the temperature was set at 1300 and 1400 °C. Moreover, the reaction temperature was increased to 1600 °C and the holding time was kept at 2 h with a silicon/zirconium molar ratio of 12. The preparation process is illustrated in Figure 1. As illustrated, with an $n(\text{Si})/n(\text{Zr})$ value of 6-10, SiCnws in nanocylinders shape were formed by heat-treating the precursor at 1500 °C for 2 h. By increasing the $n(\text{Si})/n(\text{Zr})$ value to 12, SiCnws with uneven diameters showing bead-like morphology were formed. Further increasing the silicon source in the precursor ($n(\text{Si})/n(\text{Zr})$ value of 14-16), the morphologies of the produced SiCnws would be in bamboo shape with varying nodes. For a longer holding time of 4 h, the SiCnws finally grew into hexagonal prism nanocylinders. At high temperature (1600 °C), the SiCnws in chain-like morphologies were obtained.

Phases of the samples were identified by X-Ray diffraction (XRD, Bruker, Germany). Crystalline sizes of each phase were calculated by the Scherrer equation. Contents of each phase were obtained by the Rietveld method. The structure of the ceramic samples was investigated by high-resolution transmission electron microscope (HRTEM, FEI Tecnai G2 F20 STWIN). Raman spectra were collected on a Raman spectrometer (Raman, Renishaw, UK) with its excitation wavelength at 514 nm. Separation and analysis of the Raman peaks were conducted using the peak

analyzer function of origin software.

Figure 1. Synthesis procedure of ZrB₂-ZrC-SiCnws with different microstructures

3. Results and discussion

3.1 Impact of heat-treated temperature on the formation of the products

Fig. 2 shows the XRD results of products obtained at 1300, 1400, 1500 and 1600 °C. At 1300 °C, only SiO₂ and ZrO₂ were observed, indicating that the temperature was not high enough to initiate the carbo/borothermal reduction reactions to produce ZrB₂, ZrC and SiC. As the temperature was increased to 1400 °C, SiO₂ and ZrO₂ remained the major phase, and a small amount of SiC was observed, indicating the onset temperature for SiC formation. At 1500 °C, a XRD pattern containing ZrB₂, ZrC and SiC was obtained. The peaks of SiC can be assigned to the (101), (006) and (108) reflections of 6H-SiC, among which and the (006) diffraction peak are the strongest, indicating that SiCnws mainly grew along the direction of [001]. Besides SiC, ZrB₂ and ZrC phases, no other phases were detected, which suggested that the carbo/borothermal reduction reactions were complete at 1500 °C. As the temperature was raised to 1600 °C, the intensities of SiC diffraction peaks

increased, suggesting that higher temperature may favour the generation of SiC by reducing the loss of Si-related gaseous reactants.

Figure 2. XRD results of products obtained at 1300, 1400, 1500 and 1600 °C

Fig. 3 displays the SEM results of products obtained at 1300, 1400, 1500 and 1600 °C, respectively. Since the temperature of 1300 °C was not high enough to initiate carbo/borothermal reduction reactions, a porous product with many micro-cracks was observed (Fig. 3a). Meanwhile, without the release of SiO/CO gases, there was no SiCnw grown in the product. After heat-treated at 1400 °C (Fig. 3b), the porous products remained, but dropwise projections appeared on its surface, which was ascribed to SiO₂ based on the result of EDS. Meanwhile, large quantities of wire-like SiCnws with diameters around 200 nm and lengths longer than 100 μm appeared. Combined with the XRD analysis, SiC was formed at 1400 °C, during which the generated SiO/CO gases provided the gas saturation for the continuous growth of one-dimensional SiC. And also, due to the low and periodical fluctuating gas supersaturation, the periodically fluctuated diameter of nanowires were produced. Hence, uniform and thin SiCnws in bamboo-like shape were achieved at a relatively stable growth rate. Further increasing the temperature to 1500 °C (Fig. 3c), a large quantity of SiCnws together with fine ceramic particles were obtained. The SEM image reveals the formation of fine ceramic particles in a size of about 150 nm with irregular appearance. The diameter of SiCnw varied in the range of 100-400 nm. The

length of SiCnws was over tens of microns. Moreover, unevenly distributed bamboo joints with variations in thickness were observed. At this temperature, reactions between the oxides and the carbon happened vigorously, accompanied with the generation of large quantity of SiO/CO gases and the formation of ZrB₂-ZrC-SiC phases. Because of the higher temperature and higher amount of gases, a high gas supersaturation contributing to an enhanced deposition rate and growth rate of SiC was obtained. Large fluctuations of gas saturation resulting from the rapid gas consumption lead to the nonconstant diameter in a single SiCnw. Further heat-treated at 1600 °C (Fig. 3d), an increased gas concentration and accelerated growth rate of SiC were achieved because of the increased temperature, accompanied by the formation of chain-like nanowires with lengths higher than 100 μm and diameter around 400 nm. Meanwhile, the average size of ceramic particles was about 100 nm.

Based on the above discussion, by improving the temperature from 1300 to 1600 °C, the ceramic products were transformed from porous oxides into ZrB₂, ZrC and SiC ceramics with 100 nm size. 1400 °C was high enough to provide the energy to grow one-dimensional SiCnws. The growth of SiCnws began at 1400 °C, and with the increasing of temperature, the morphology of SiCnws evolved from bamboo-like shape (diameter around 150 nm) into chain-like shape linked by polyhedra (diameter around 400 nm).

Figure 3. SEM results of products obtained at different temperatures

3.2 Impact of holding time on the formation of the products

Fig.4 demonstrates the XRD results of the products prepared at different holding times at 1500 °C. After heat treatment at 1500 °C for 1 h, only ZrB_2 and SiC phases were detected, indicating that the reaction was not completed to produce ZrC. Diffraction peaks assigned to ZrC appeared with extending holding time of 2 h. With prolonged holding time, besides the sharpened diffraction peaks and increased peak intensities, no other changes were observed from the XRD patterns. Based on the phase composition of the products in Fig.5a, the content of SiC, ZrB_2 and ZrC phases

did not change significantly with extending the holding time from 2 to 4 h, indicating that the reactions to produce the above phases were completed for two hours of holding time. When further increased the holding time, phase composition of the products kept unchanged, except for the improved crystallinity. Fig.5b shows the apparent crystal size of each phase in the products obtained from various holding times. It shows that with extending holding time, the crystal size of each ceramic phase tended to decrease.

Figure 4. XRD results of the products with different holding times

Figure 5. The content (a) and the crystal size (b) of key phases in the products with various holding times

Fig.6 displays the SEM results of the products from the precursors with

different holding times. After thermal treatment at 1500 °C for 1 h, because of the short holding time, the reactions were not completed, and only a low concentration of reactant gases was produced. Under this condition, the growth of SiCnws was favoured, and a large quantity of long SiCnws was observed. Meanwhile, the ceramic particles mainly composed of cubic ZrB₂ particles. With prolonged holding time of 2 h, large amount of SiCnws with a length up to 100 microns were found to disperse uniformly in the ceramic products. Combined with the analysis of XRD, the carbo/borothermal reduction reactions seemed to be completed with a holding time of 2 h, during which the gas concentration reached its maximum. Due to the increase amount of reactant gases and high temperature, the energy of gas molecules, their migration and collision frequencies are increased, and a larger gas supersaturation was obtained. Since the nucleation is proportional to the supersaturation degree, a large amount of SiC crystals were formed. And then, with a relatively higher degree of gas supersaturation, a high nucleation and growth rate lead to the formation of large amount of SiCnws with uneven diameters and shorter lengths. With a holding time of 3 h, a large amount of SiCnws were distributed in the product, showing smaller diameters and longer lengths. Compared to two hours of holding time, the particle size of ceramic powder was reduced. With the prolonging of holding time, the gas concentration was further diluted by the growth of large SiC crystals. The growth of SiCnws was maintained by a low but stable gas supplement, and reached lengths higher than 100 um. When holding at 1500 °C for 4 h, only a few SiCnws was observed in the product. The uniform ceramics with an average size around 50nm were obtained. With an excessive holding time (4 h), the growth of SiCnws was strongly suppressed. The above analysis confirmed that the continuous growth of SiCnws was supported by a relatively low supersaturation Σ , which is controlled by the partial pressure of SiO and CO gases, i.e., $\Sigma = k \cdot P_{\text{SiO}} / P_{\text{CO}}$. k represents the equilibrium constant of the reaction to form SiC, i.e., $\text{SiO (g)} + 3\text{CO (g)} = \text{SiC (s)} + 2\text{CO}_2 \text{ (g)}$. When supersaturation exceeded the adaptable range, the SiC phase in the form of particles was favoured. Due to the over-consumption of gases through the generation of large SiC crystals during the holding period, the degree of gas

supersaturation was too low to keep the growth of one-dimensional SiC. Therefore, just a small amount of SiCnws was formed under the over-reduced gas saturation.

Figure 6. SEM results of the products from the precursors with different holding times

The reason for the morphological evolution of the SiCnws during the prolonging of holding times can be explained as follows. The shape of the grown 2D nuclear lay

on the competition between the kinetic conditions and the minimization of surface and line energies [40]. With a low and fluctuating gas saturation, the growth of SiCnws in hexagonal and cylindrical shape grew competitively, forming this metastable shape of nanowires with holding time of one hour. Improving the holding time to 2 h, the gas saturation increased dramatically, accompanied by an increase in growth rate, thus contributing to the generation of altering hexagonal or hexagonal-like and cylindrical shape. Since an angle of about 141° is formed between the two adjacent $\{111\}$ facets of hexagonal shape, the and compressive and tensile stresses may be caused by the growth of SiCnw. In the following process, bamboo-shaped nanowires were formed resulted from the promoted growth at the dilated region and inhibited growing at the compressive region. Further increasing the holding time, full rearrangements of atom was better achieved, and the nanowires grew into hexagonal with lower specific line energy.

3.3 Impact of holding time on the structure order of SiCnws

Fig.7 shows the Raman spectra and fitted Raman peaks of the SiCnws from the products with different holding times. In Fig.7a, there are two Raman peaks of 796 cm^{-1} (transversal optic mode of SiC, TO) and 968 cm^{-1} (longitudinal optic mode of SiC, LO) existed. The appearance of a shoulder peak located at around 765 cm^{-1} may be raised from the stacking faults of the SiCnws. Based on the phonon-confinement model, a smaller nanocrystal size and larger disorder will contribute to Raman scattering, thus leading to a broadening and downshift of the peaks [41]. Compared with that of the other samples, the TO and LO modes shift from about 796 to 779 cm^{-1} and from about 960 to 950 cm^{-1} for the SiCnws with a holding time of 2 h, indicating a high structure disorder in this sample.

In the spectra of SiCnws with holding times from 1 h to 4 h, the LO mode intensity decreases, gradually lowering than that of TO. According to previous reports, the LO mode intensity is always weaker than that of the TO mode, as a result of the suppression effect arising from the imperfect or disordered microstructures [42]. Whereas, the quantum confinement or defects as a result of the inner stress during the crystal growth is believed as the reason for a high LO mode. Moreover, smaller LO

mode intensities are related to the size decrease of the SiC nanostructures. With a larger nanocrystal, the enhanced LO mode intensity will be detected [43]. Based on the above analysis, it can be inferred that the amount of structural defects reached the highest level with a holding time of 2 h, and then decreased by prolonging the holding time. Meanwhile, as the holding time increases, the size of the SiC microcrystals was gradually decreased, as verified by the calculated grain size in Fig. 5b.

Figure 7. Raman spectra (a) and the fitted Raman peaks (b) of the SiCnw from the products with different holding times

Moreover, the ratio of the shoulder peak intensity to the one at 784 cm⁻¹ suggests the proportion of defects versus the SiC crystallines. And the frequency separation between the TO peaks and its shoulders can reflect the average distance between stacking faults [44]. In Fig.7b, the intensity ratio of the shoulder peak to TO peak (I₁:I₂) increases, and the frequency separation between these two peaks (Δx) decreased as the holding time was extended from 1 h to 2 h, indicating an increased structure disorder. Prolonging the holding time to 3 h, decrease of the relative intensity and increase of the frequency separation suggest that prolonging the holding time would contribute to an reduced structure disorder. Whereas, the degree of the structure order decreased with an excessive holding time of 4 h.

3.4 Impact of silicon content on the composition and morphology of the products

Fig.8 presents the XRD results of the samples obtained at 1500 °C using various amounts of silicon source. As can be seen, all the samples had a composition of SiC, ZrB₂ and ZrC. With increasing of the silicon content, peak intensity of SiC continually increased, and relative peak intensities of ZrB₂/ZrC first decreased and

then increased. Based on the phase compositions shown in Fig.9, SiC (52 wt%), ZrB₂ (33 wt%) and ZrC (13 wt%) were detected in the obtained product with a Si/Zr molar ratio ($n(\text{Si})/n(\text{Zr})$) of 6. With the increase of the $n(\text{Si})/n(\text{Zr})$ value, the content of SiC continually increased, and the relative content of ZrB₂/ZrC decreased gradually on the whole. When $n(\text{Si})/n(\text{Zr})$ reached 16, SiC (78 wt%), ZrB₂ (11 wt%) and ZrC (11 wt%) were identified. By analyzing all the products, it is found that all the phase contents were lower than the theoretical SiC: (ZrB₂ and ZrC) weight ratio of the samples, indicating that a certain amount of gaseous reactants (SiO, CO) was escaped during the reactions. Moreover, the higher evaporation loss of B₂O₃ as a result of the refinement ceramic particles (confirmed by the following SEM analysis) contributed to the decreased amount of ZrB₂. Meanwhile, the reactions between the oxides and the carbon phase to form these ceramic products became more intensive due to the same reason.

Figure 8. XRD results of the products with different silicon contents

Figure 9 The content of key phases (a) and the average diameters of SiCnws (b) in the products with different silicon contents

Figure 10. SEM results of the products with different silicon contents (a, a₁, a₂) 6 ≤ n(Si)/n(Zr) < 10, (b, b₁, b₂) 10 ≤ n(Si)/n(Zr) < 14, (c, c₁, c₂) 14 ≤ n(Si)/n(Zr) < 16

Fig.10 demonstrates the SEM results of the products prepared from precursors with different silicon contents. The average diameters of SiCnws in these products were shown in Fig.9b. The amount of SiCnws grown in the product increased with increasing n(Si)/n(Zr) value. When the n(Si)/n(Zr) value reached 16, the growth of

nanowires was suppressed. Moreover, besides the gradually increased length of the nanowires, the average diameters of SiCnws increased first and then decreased (as seen in Fig.9b). In addition, an obvious refinement of ceramic particles, i.e. the mean particle size decreased from about 500 nm to around 150 nm, can be observed, verifying the refining functions of SiC [45]. For the morphologies of the grown SiCnws, from the precursor with a low $n(\text{Si})/n(\text{Zr})$ value (Fig. 10a), only a few short but uniform SiCnws were observed due to the insufficient concentration of reactant gases. Further increasing the silicon content (Fig. 10b), the concentration of reactant gases increased, and the growth of SiCnws was supported with a higher but fluctuating gas supersaturation. Therefore, the diameter of a single SiCnw increased, and a bead-like morphology was obtained. At an excessive silicon content, the growth of SiCnws was restricted due to the excess gas supersaturation. The formation of large SiC crystals was favoured initially and then the SiCnws grew in the product under reduced gas supersaturation. And a bamboo-like morphology (Fig.10c) was obtained as a result of the gradually stabilized growth rate of the radical direction in the SiCnws.

3.5 Impact of silicon content on the structure order of SiCnws

Fig.11 presents the typical Raman spectrum of the SiCnw with different $n(\text{Si})/n(\text{Zr})$. TO and LO modes positioned at around 784 cm^{-1} and 956 cm^{-1} were detected, and a shoulder peak appeared at the center of 756 cm^{-1} corresponding to the stacking faults of SiCnws. Compared with bulk SiC with narrow diffraction peaks, all the peaks of SiCnws exhibited a broadening and asymmetry characteristic, which was believed to be caused by the size confinement effects and planar faults. Moreover, an obvious red shift was observed with increasing $n(\text{Si})/n(\text{Zr})$ value, suggesting a decreasing nanocrystal size and increasing structure disorder. Based on the analysis of fitted Raman peaks, it can be seen that the TO line shifted to lower frequencies and was broadened with the increasing $n(\text{Si})/n(\text{Zr})$ value. Furthermore, the relative intensity of the shoulder peak to TO peak ($I_1:I_2$) increased, along with the decreased frequency separation between these two peaks, i.e. a decreasing average stacking fault distance (L), verifying an increased disorder in the products with higher silicon

content.

Figure 11. Raman spectra (a) and the fitted Raman peaks (b) of the SiCnw from the products with different silicon contents

3.6 Mechanism discussion

Fig.12a shows the TEM results of the products annealed at 1500°C with a $n(\text{Si})/n(\text{Zr})$ value of 12, which reveals a uniform size distribution of 50-100 nm. Fig.12b, 12c and 12e show the typical images of the prepared nanowires with different morphologies, and the diameters ranges from ~ 100 nm to ~ 250 nm. The morphology of nanowires includes uniform, straight and long linear structure (Fig.12b), linear shape with a thicker node (Fig.12c), as well as short and spiral shape (Fig.12e). Moreover, no metal catalyst existed at the tip of the grown nanowires, indicating the SiCnws were formed via the typical VS mechanism. From the HRTEM in Fig. 12d, the (006) fringes are divided by about 0.254 nm averagely, inferring that the single crystalline SiCnw grew along the [001] direction. The SAED pattern (the inset of Fig.12c) indicates a feature of a single-crystal structure. Fig.12f reveals the existence of stacking faults and planar defects with high density in the spiral shape SiCnw (denoted by the white arrows in Fig. 12f). The HRTEM image of the spiral shape SiCnw also shows a growth direction of [001] (indicated by the black arrow in Fig. 12f). While, the adjacent facets form a 146.2° angle, suggesting the existence of growth stress, which may be a metastable shape. Moreover, the evolution of morphologies verifies the variation of gas saturation in the growth region of SiCnws, which was determined by the competition between supplement of reaction gases (SiO and CO) released from the carbothermal reduction reactions and the formation rate of

SiC. Especially, in the multiphase system, the reactions to produce SiC, ZrB_2 and ZrC are crucial to determine the morphology of SiCnw, which will be discussed in the next section.

Figure 12. (a,b) TEM results of ZrB₂-ZrC-SiC ceramic powder, (b) TEM image of SiCnw in nano-cylinder shape, TEM (c) and HRTEM (d) results of SiCnw with fluctuating diameters and the corresponding SAED pattern (the inset of c). TEM (e) and HRTEM (f) results of SiCnw with high content of stacking faults

The growth process of ZrB₂-ZrC-SiCnw is demonstrated as follows, and the influences of each factor on the morphology evolution of the SiCnws were illustrated in Fig.13. Firstly, SiO and CO gas sources were produced with the reduction of SiO₂ and CO₂ through reactions (1)-(3) [46]. SiC embryos were formed from heterogeneous nucleation by the solid-gas interaction of reaction (4), but the growth of SiC nanowires is determined by reaction (5) with gas-gas interaction [47,48]. As observed, the growth of SiCnw is decided by the separate partial pressure of CO and SiO vapour. At the same time, ZrB₂ and ZrC were generated through reactions (6) and (7), respectively, accompanied by the release of gaseous CO.

The growth of SiCnw was achieved through reaction 5, in which the CO gases was hard to get saturated. The irregularities along the axis of nanowires were resulted from the fluctuation in the partial pressure of gaseous CO. Since slight variation in the gaseous will influence violently the growth of SiCnws, the CO gas generated from the bro/carbothermal reactions to form ZrB₂/ZrC ceramics has an impact on the local supersaturation of the SiO and CO vapors. Below the formation temperature of ZrB₂ and ZrC ceramics (Fig.13a), e.g. 1400 °C, SiCnws in nanocylinders shape were formed since the precipitation rate of SiC was approximately equal to the adsorption rates of gaseous CO and SiO. As shown in Fig.13b, for the sample with an n(Si)/n(Zr) value of 10-12, when heat treated at 1500 °C, i.e., the formation temperature of ZrB₂ and ZrC ceramics, as the concentration of CO reached high supersaturation during the heating, structural defects or imperfections reached the highest level with preservation time 2 hours and the SiCnws showed a bead-like morphology. With extended holding time, the defects were reduced and the SiCnws finally grew into hexagonal

nanocylinders. Variations in silicon source of the precursor, seen in Fig.13c, i.e. the raw material contents participated in the reactions to form SiC, mainly caused remarkable changes in the length of nanocylinder SiCnw, while the morphologies of the SiCnws would be more or less maintained, except for the variations in diameter fluctuation range of the single SiCnw. At higher temperature (Fig.13a), however, e.g. 1600 °C, the SiCnws became energetically favorable hexagonal after the fully atom rearrangements.

(a) Influence of temperature on the growth of SiCnws

(b) Influence of holding time on the growth of SiCnws

(c) Influence of n(Si)/n(Zr) in the precursor on the growth of SiCnws

Figure 13. Schematic illustrating the influence of different factors on the morphology evolution of SiCnws

4. Conclusions

In summary, this work provided a simple method of in-situ fabricating uniformly dispersed SiCnws with various special morphologies in ZrB₂-ZrC nanopowders was proposed. The prepared SiCnws had a diameter of varying from 100 to 400 nm, and

the morphologies of SiCnws included nanocylinder, bamboo-shape with tunable nodes, chain-like and hexagonal prisms, with the length of which varies from tens to hundreds of microns. The formation of ZrB₂-ZrC-SiC phases occurred at temperatures over 1500 °C. The obtained ceramic powders were in a nanoscale of about 100 nm. The CO gas generated from the bro/carbothermal reactions to form ZrB₂/ZrC ceramics shows an obvious impact on the local supersaturation of the SiO and CO vapors, thus leading to formation of SiCnws with specific morphologies. The in-situ grown SiCnws with specific microstructures, and the controllable morphologies opens up a new opportunity for fabricating high-performance ceramic composites.

Notes

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