

Chemical Reactions, Anisotropic Grain Growth and Sintering Mechanisms of Self-Reinforced ZrB₂-SiC Doped with WC

Ji Zou,^{‡,§} Shi-Kuan Sun,^{‡,§} Guo-Jun Zhang,^{*,†,‡} Yan-Mei Kan,[‡] Pei-Ling Wang,[‡] and Tatsuki Ohji^{**,¶}

[‡]State Key Laboratory of High Performance Ceramics and Superfine Microstructures, Shanghai Institute of Ceramics, Shanghai 200050, China

[§]Graduate School of the Chinese Academy of Sciences, Beijing 100049, China

[¶]National Institute of Advanced Industrial Science and Technology, Nagoya, Aichi 463-8560, Japan

Transmission electron microscopy study of pressureless sintered ZrB₂-20 vol% SiC composites with WC (5-10 vol%) additions was carried out in this work. Two independent chemical reactions in which the ZrO_2 impurities were removed from ZrB_2 grain surface were confirmed. Three new formed phases, (W, Zr)_{ss}B, (Zr, W)ssC, and (W, Zr)ssSi2, apart from the plate-like ZrB2 and SiC grains, were identified in the samples. Microstructure observations strongly suggest that the liquid phases in terms of (W, Zr)_{ss}B and (W, Zr)_{ss}Si₂, appear in this system during the sintering process below 2200°C, and the former could well wet the ZrB₂ grain boundaries. The mass transport process between ZrB₂ and (W, Zr)_{ss}B was also confirmed by scanning-transmission electron microscope analysis. The above results supports that the densification at 2200°C is assisted by liquid phase and the elongation of ZrB₂ platelets resulted from the Ostwald ripening during the dissolution-diffusion-precipitation process.

I. Introduction

 $S^{\rm IC-REINFORCED} \ ZrB_2 \ composites \ (normally \ with \ 10-30 \ vol\% \ SiC \ in \ particulates \ or \ whiskers \ forms^{1-3}) \ have \ a \ series \ of$ excellent properties, such as high bending strength (500– 1000 MPa),^{1,3–4} high oxidation resistance,^{5,6}moderate tough-ness, (3.5–6 MPa \cdot m^{1/2}) and high hardness (18–20 GPa).^{1–4,7} The addition of SiC lowers the melting point of ZrB₂-based system from about 3200° to 2320°C,⁸ ZrB₂–SiC system has been drawing great attention since recent years due the combination of properties mentioned above and its potential applications in hypersonic technology. For instance, it could serve as thermal protection materials for sharp leading edges in reusable launch vehicles as well as for hypersonic flight.

Because of the poor sinterability of ZrB2 and SiC, their condensation was typically accomplished by applying pressures (20–30 MPa) at high temperature (1800°–2000°C).⁴ Hot press sintering indeed has some advantages, but it poses a number of problems in the fabrication of complex components, which restricts the applications of ZrB₂–SiC under the engineering aspect.

To solve this problem, various sintering aids have been added into ZrB₂ in order to enhance its pressureless densification. The ceramics mainly used as sintering aids can be divided

into two categories: (1) transition metal silicides ($MoSi_2$, $ZrSi_2$, $TaSi_2$),^{10–12} whose densification effect was thought to be the formation of a liquid phase, which can accelerate the mass transportation process between ZrB_2 grains; (2) carbon and carbides (WC,¹³ B₄C,¹⁴ and B₄C–C¹⁵), which react with and remove the oxides layer on the surfaces of the starting ZrB₂ particles.

Among the second group of the sintering aids, tungsten carbide (WC) is of great interest, due to the multiple and beneficial effects under various aspects, which are summarized as follows. First, the highest four-point bending strengths (over 1 GPa) in ultra-high temperature ceramics (UHTCs) at room temperature were reported in ZrB₂-SiC-WC composites.¹ Second, WC can improve the oxidation resistance of ZrB₂ by forming WO₃-ZrO₂ liquid phase on its surface oxide layer during oxidation at moderately high temperature.¹⁶ Third, WC is conducive to the formation of elongated ZrB2 grains,7 and ZrB2-SiC with this unique interlocking microstructure possesses high toughness (6.5 MPa \cdot m^{1/2}) compared with the common ones $(3-4 \text{ MPa} \cdot \text{m}^{1/2}).^{17}$

In addition, cobalt-bonded WC milling media is widely uti-lized to grind ZrB₂ powders.^{13–15}Owing to the hardness difference between WC and ZrB₂, WC could spontaneously be added into ZrB₂ powders during this milling process. On the other hand, oxide impurities, in terms of ZrO_2 and B_2O_3 , are always present on the surface of ZrB_2 .¹⁸ Unlike B_2O_3 , most of which could be removed from the starting powders through its evaporation at temperatures above 1300°C in vacuum furnace during sintering, ZrO₂ removal is more difficult. The external ZrO₂ made the chemical reactions in ZrB2-SiC-WC systems more complex. Though WC is considered as an effective sintering aid for ZrB₂, the reactions among ZrB₂, SiC, WC, and the effective role of WC on the densification and the elongation of ZrB2 grains are not fully clarified.

Several investigations have proved that the reaction between WC and ZrO_2 could occur,¹⁴ and these results could explain why WC enhances the densification of ZrB₂. The reaction between WC and ZrB2 was also observed. However, neither specific product, nor reaction path was identified.^{1,7} In our previous report⁷ based on energy-dispersive spectroscopy (EDS) analysis, we speculated about the occurrence of a displacement reaction between WC and ZrB₂, but the identification of the phase products was restricted by the experimental conditions.

How does WC react with ZrB₂? Are the reaction products the solid solution of Zr in WB as well as W in ZrC as assumed? What is the morphology of the ZrB₂ grains, rod or platelet? What is its growth direction? Why could WC favor the densification and elongation of ZrB₂ grains? These issues were connected with the high toughness of self-reinforced ZrB2-SiC-WC-based ceramic.⁷ A thorough investigation on them could optimize the sintering aids utilized for the acceleration of the anisotropic growth of ZrB2 grains, which is a new way to

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[†]Author to whom correspondence should be addressed. e-mail: gjzhang@mail.sic.ac.cn **Fellow, The American Ceramic Society

Material	Particle size (D_{50}) (µm)	Impurities (%)	Supplier
Received ZrB ₂	14	O 0.5, Na 0.01, Al 0.01, Ca 0.06, Fe 0.2, Si 0.01, Hf 1.5, Ti 1.9, V 0.01	Sanxing Ceramics Materials Co., Ltd., Gongyi, China
Milled ZrB ₂	1.4^{\dagger}	O 1.7, others were not analyzed	The same
α-SiC	0.45^{\dagger}	B 0.33, O 1, Ca 0.24, Cl 0.1, Fe 0.16, V 0.09	Xinyuan Carborundum Co., Ltd., Changle, China
WC	$< 1^{\dagger}$	C6.13, Cr 0.03, Co 0.01, Mo 0.01, O 0.2	Hard alloy Co., Ltd., Zhuzhou, China
ZrO ₂	0.3^{\dagger}	NA	CSG Holding Co., Ltd., Shenzhen, China

Table I. Characteristics of the Raw Materials

[†]From the supplier. NA, Not analyzed.

realize high toughness in UHTCs. To this end, observations on a small length scale are required, which are the preferential advantages of high-resolution transmission electron microscopy (HRTEM). However, the studies to use HRTEM to analyze the microstructure of sintered UHTCs are very few.^{19,20} So in this paper, we investigated the chemical reactions, phase formation and microstructure evolutions of the ZrB₂–SiC–WC composites prepared by pressureless sintering by HRTEM. The mechanisms for the formation of such a tough interlocking microstructure in ZrB₂–SiC ceramics are thoroughly discussed.

II. Experimental Procedure

Commercially available powders of ZrB_2 , SiC, and WC were used as the raw materials. The main impurities, particle size, and suppliers are listed for the powders in Table I. Five and 10 vol% WC-doped ZrB_2 -20 vol SiC composites (ZSW5, ZSW10) were prepared by pressureless sintering at 2000°-2200°C for 2 h. The whole sintering schedule included an external isothermal holds at 1650°C in vacuum, and then argon gas was introduced into the furnace. The details of the processing and sintering procedures have been shown elsewhere.⁷



Fig. 1. Scanning electron micrograph of ZSW5 (a) and ZSW10 (b) sintered at 2200°C. EDX spectra from selected points A and B in (b) were shown in (c) and (d), respectively.



Fig. 2. The XRD pattern of ZrB_2 —20 vol% SiC—10 vol% WC sintered at 2200°C, the position of ZrB_2 peaks (JCPDF 34-0432) was arrowed.

Powder mixtures of ZrB_2 –WC (ZW) and ZrB_2 –WC–ZrO₂ (ZWO) were pressed and used to investigate the chemical reactions as well as the sintering mechanism. Their ratios were set as 1:1 and 3:6:1, according to the possible reactions which are discussed in the Section III(2). These additional pellets were heated in vacuum at 1450°, 1650°, or 1850°C for 1 h.

The phase analysis of the as-sintered samples and additional pellets was conducted by X-ray diffraction (XRD; D/Max-2250 V, Rigaku, Tokyo, Japan) using CuK α radiation. The microstructures of the polished surface were examined by SEM (JXA-8100, JEOL, Tokyo, Japan) with EDS (Oxford Instruments, Oxford, U.K.), and all the acceleration voltages were set as 10 keV. Commercial software package (HSC Chemistry 6.1) was used to perform the thermodynamic calculations. The grain size and the aspect ratio of ZrB₂ grains were measured on an average of 100 grains by the software of Image Pro-plus.

The transmission electron microscopy (TEM) samples preparation was performed by standard techniques, which included mechanical grinding, polishing, dimpling, and finally ion thin-

Table II. Typical Distance of Planes in (W, Zr)_{ss}B and (Zr, W)_{ss}C Derived from Electron Diffraction and Refined X-Ray Diffraction (XRD) Compared with the Corresponding Values in Pure WB and ZrC

The planes of (W, Zr) _{ss} B	Intensity	From electron diffraction (nm)	From XRD refinement (nm)	From JCPDF card 35-0738				
(112) (103) (105) (200)	100 90 87 26	0.216 0.276 0.231 0.158	† 0.2740 0.2302 0.1566	0.2133 0.2727 0.2291 0.1558				
The planes of (Zr, W) _{ss} C	Intensity	From electron diffraction (nm)	From XRD refinement (nm)	From JCPDF card 35-0784				
(111) (200) (220) (311)	100 90 62 50	0.270 0.233 0.164 0.140	0.2675 0.2316 0.1638 0.1397	0.2708 0.2345 0.1659 0.1414				

The error level of the data collected by electron diffraction and XRD refinement were 10^{-3} and 10^{-4} nm, respectively. [†]The peak was overlapped.

ning. The phase analysis and characterizations were performed using a 200 kV TEM (JEM2100, JEOL), which is equipped with an X-ray energy-dispersive detector systems (EDS Model Link-ISIS, Oxford Instruments) and an appurtenance of scanningtransmission electron microscope (STEM). The minimum analyzed spot sizes of EDS were 10 nm and the atomic ratios of interested elements are calculated according to the Cliff– Lorimer equation from the acquired EDS spectra.

III. Results and Discussion

(1) Microstructure and Phase Identification

The typical polished surfaces of ZrB_2 -SiC with different amounts of WC are shown in Figs. 1(a) and (b). Besides ZrB_2 and SiC, the microstructure contains two extra phases. According to the chemical analysis from the EDS in Figs. 1(c) and (d) and the slight peak shifts in the XRD pattern (Fig. 2), these



Fig. 3. (a) Bright field TEM image showing faceted ZrB_2 grains surrounded by (Zr, W)_{ss}C and (W, Zr)_{ss}B, (b)–(d) and (e)–(g) are the corresponding electron diffraction patterns recorded at different tilting angles and indexed as ZrC and WB.



Fig. 4. TEM image of two typical ZrB_2 palates (a) and (c), Inset: their corresponding SAED patterns; The HRTEM (b) and (d) show preferential growth directions of the elongated ZrB_2 palates in (a) and (b), Inset: the preferential growth direction and the crystal morphology of ZrB_2 palates.

peaks have been indexed to $(W, Zr)_{ss}B$ and $(Zr, W)_{ss}C$.⁷ This assumption is different from Chamberlain's work, which were indexed to WC and unknown phase.¹ In order to verify our hypothesis, detailed phase identifications were conducted by

selected area electron diffraction (SAED) with different tilting angles from one single $(W, Zr)_{ss} B$ or $(Zr, W)_{ss}C$ grain, as shown in Figs. 3(b)–(g). Their typical crystal plane spacing was calculated as shown in Table II. They are consistent with the XRD



Fig. 5. EDS (a) and SAED (b) patterns of $(W, Zr)Si_2$ phase.



Fig. 6. Change in the Gibbs' free energy of reaction as a function of temperature for reactions ((1)-(3), (5)).

refinement, slight higher (in (W, Zr)_{ss}B case) or lower (in (Zr, W)_{ss}C case) than those from the corresponding values in JCPDF cards, due to the solid solution effects. Furthermore, these patterns (Figs. 3(b) and (f)) of low-indices basic zone axes are substantially similar with that in pure ZrC (F_{m3m}) and WB ($I4_1/amd$). Combined with XRD analysis, the above results showed that the incorporation of Zr did not significantly change the crystal structure of WB, due to the approximation of the atomic radii. Similar phenomenon also occurred to ZrC. No ternary or other phases containing W–Zr–B–C were identified.

Both the SiC and ZrB_2 grains in ZSW5 and ZSW 10 are elongated. SiC grains are similar in these two samples, while the sizes of ZrB_2 are different. The elongated ZrB_2 grains in ZSW10 are nominally 10–30 µm long, with an aspect ratio of 3.8, higher than those of ZSW5, which are 5–15 µm and 2.9, respectively.

Some typical TEM images of such ZrB_2 grains are shown in Fig. 4. Most of their interfaces are planar with clear lattice fringes. Two kinds of typical interlayer distances (0.275, 0.159 nm) were measured from 20 randomly selected elongated grains, which are consistent with the interplanar distance of the (100) and (110) planes of ZrB_2 , respectively. The SAED pattern of corresponding grains can be indexed as [010] and [110] zone spots (inset Figs. 4(a) and (c)). These results mean that ZrB_2 grains have two preferential growth direction,²¹ [210] and [110] (as illustrated inset in Fig. 4(b)), which form a two dimensional network. Hence, the real morphology of ZrB_2 grains are plate rather than rod in the ZSW10 sample sintered at 2200°C.

 ZrB_2 grain tend to grow with *c*-axis perpendicular to the plate plane, because the fastest growing planes of the IVa group diboride (ZrB₂, HfB₂, and TiB₂) are the {010}{110} families and the low-activation energy diffusion path is along $\langle 210 \rangle$ and $\langle 1-10 \rangle$ direction. Both of them are consistent with the growth direction obtained from floating zone growth of ZrB₂²¹ or HfB₂²² single crystals. Similar grain growth behavior was also observed in ZSW5 sintered at 2200°C.

Apart from the phase mentioned, a new type of crystalline phase was also detected in this study. The chemical analysis of this impurity by EDS (Fig. 5(a)) showed that the average composition of the unknown phase was: W: 27 at.%, Zr: 8 at.%, and Si: 64 at.%.

In the W–Si binary phase diagram, only two thermodynamic favorable compounds exist. One is W_5Si_3 , and the other is WSi_2 . The *d*-values calculated from the SAED (Fig. 5(b)) show that the distances of the (002) and (010) planes of the unknown phase are 0.413 and 0.316 nm, slightly higher than those in WSi_2 (JCPDF 11–0195), which are 0.391 and 0.297 nm. The covalent radius difference between W (1.42 Å) and Zr (1.60 Å) is quite small. According to Hume–Rothery rule, we assume that a substitution of Zr to W occurred within the unit cell. The incorporation of Zr with a larger covalent radius atom into WSi₂ crystal lattice resulted in the expansion of the unit cell. On the other hand, the ratio (W+Zr)/Si in the unknown phase was equal to 1.8, which was very close to WSi₂ (2), but far deviated from W_5Si_3 (0.6).

All the above discussions support that the unknown phase is a solid solution, $(W, Zr)_{ss}Si_2$, in accordance with the XRD result of ZrB_2 -SiC-WC composites obtained at lower sintering temperature.⁷

(2) Reaction Path

The only reaction that has been confirmed in the ZrB_2 – ZrO_2 – SiC–WC systems is between WC and ZrO_2 , with formation of ZrC and W, reaction (1).^{13–14}

$$3WC + ZrO_2 = ZrC + 3W + 2CO(g)$$
⁽¹⁾

However, according to reaction (1), the amount of ZrO_2 (1.9 mol%) in the current work is not sufficient to consume all the added WC (11.5 mol%). Based on the reaction products of WB and ZrC as identified, the other possible way to consume the excess WC by reaction with ZrB_2 , reactions the following reactions:

$$5 ZrB_2 + 4WC + C = 5ZrC + 2W_2B_5$$
(2)

$$ZrB_2 + 2WC = ZrC + 2WB + C$$
(3)

The changes of Gibbs free energy (δG_m) for the reactions concerned, as a function of temperature, have been plotted in Fig. 6. From Fig. 6 it is visible that reactions (2) and (3) could not occur below 2200°C. It is noticed that carbon appears as a product in reaction (3) and carbothermal reduction of ZrO₂ (reaction (4)) has a very large, negative δG_m at lower temperature and pressure. If reactions (3) and (4) were merged and ZrO₂ was

 Table III.
 Summary of XRD Results for the Mixtures Containing: (1) 50 Vol% WC and 50 Vol% ZrO2¹⁴; (2) ZrB2; and WC (Mole Ratio 1:1); (3) ZrB2, WC, and ZrO2 (Mole Ratio 3:6:1), Sinterd at Different Tempreatures for 1 h in Vacuum

		Sintering temperature				
System	Reactions	Room temperature	1450°C	1650°C	$1800^{\circ}C^{\dagger}$	
WO	$3WC+ZrO_2 = ZrC+3W+2CO$	WC/s, ZrO ₂ /s	WC/s, ZrO _s /s W2C/w	W, ZrC, WC, W ₂ C, ZrO ₂	W, W_2C/tr ZrC, ZrO ₂	
ZW	$ZrB_2+2WC = ZrC+2WB+C$	ZrB ₂ /s, WC/s	ZrB_2/s , WC/s	ZrB ₂ /s, WC/s ZrC/vw, WB/vw	$ZrB_2/s, WC/s$ ZrC/s, WB/s	
ZWO	$3ZrB_2+6WC+ZrO_2 = 4ZrC+6WB+2CO$	ZrB ₂ /s, WC/s ZrO ₂ /s	ZrB ₂ /w, WC/w ZrC/w, WB/s	ZrB ₂ /vw, ZrC/s, WB/s, unknown/w	ZrC/s, WB/s	

[†]1850°C for the reaction between WC and ZrO₂ in Zhang et al.¹⁴ s, strong; w, weak; vw, very weak; tr, trace.



Fig. 7. XRD patterns for the powder mixtures containing (a) ZrB_2 and WC (molar ratio 1:1); (b) ZrB_2 , WC and ZrO_2 (molar ratio 3:6:1) sintered at different temperatures in vacuum for 1 h. The dotted arrows indicated more W was incorporated into ZrC phase when temperature elevated.

added into reaction (4), the favorable reaction temperature between ZrB_2 and WC (reaction (5)) will be decreased remarkably.

$$ZrO_2 + 3C = ZrC + 2CO(g)$$
(4)

$$3ZrB_2 + 6WC + ZrO_2 = 4ZrC + 6WB + 2CO(g)$$
 (5)

Thermodynamic calculations confirmed the above speculations. Reaction (3) in the ZW system is favorable above 2300° C, while the reaction (5) in ZWO system is favorable above 1807° C in standard state. Furthermore, a mild vacuum (about 5 Pa) was maintained during the first sintering stage, which would decrease the favorable temperature of reaction (5), from 1807° C at 1 atm to 1234° C at 5 Pa. Because no gaseous phase is released from reaction (3), the vacuum will not affect the reaction temperature in ZW systems.

To verify the occurrence of the above mentioned reactions, powder mixtures (Table III) were heated at lower temperature, to analyze the crystalline phases formed at 1450°, 1650°, and 1850°C. Stacked XRD patterns of the starting compacts and those treated at different temperatures are presented in Fig. 7. The phases formed during 1 h isothermal holds at different temperatures have been summarized and compared in Table III. The reaction between ZrB₂ and WC is really difficult. In ZW, besides ZrB₂ and WC, no other phases were observed until the temperature reached 1650°C, and the reaction was not completed even after isothermal holds at 1800°C. In ZrO₂-WC systems, WC seems to decompose to W₂C and C first. Though WC appears effective for removing ZrO2, traces of W2C were still observed after permanence at 2100°C. The most effective way for removing ZrO₂ appeared in ZWO, in this system, WB and ZrC were formed and changed to the major phases at the temperature as low as 1450°C. After the holding at 1800°C, only WB and ZrC were left. Furthermore, the peak shift (at 55.323° for ZrC (220)) in ZWO increased with the temperature (as arrowed in Fig. 7(b)), indicating the formation of $(Zr, W)_{ss}C$ at the same time.^{23,24}

 ZrO_2 , well known as impurity in borides, served as a catalyst, which accelerates the reaction between WC and ZrB_2 . Based on the above analysis, two different reaction paths of WC in ZrB_2 (ZrO_2)–SiC can be imagined: (a) when enough ZrO_2 exists on the surface of starting ZrB_2 particles, WC will first react with ZrO_2 to form ZrC and W as indicated by reaction (1); (b) when limited ZrO_2 was around the ZrB_2 grains, the ternary reaction between ZrB_2 , WC and ZrO_2 takes place, and thus WB and ZrC can be found in the sample according to reaction (5).

The as-formed W from reaction (1) could either react with SiC to form WSi_2 or could be incorporated into the ZrB_2 or ZrC lattice, as confirmed by XRD patterns and EDS results.

(3) Sintering Mechanisms and Formation of Interlocking Microstructure

Some important conclusions explored in the present and previous investigations, which are relevant for the development of the ZrB_2 grains and the sintering mechanisms, are summarized as follows:

(i) Elongated ZrB_2 grains formed when WC was added. However, the same morphology configuration did not appear in the ZrB_2 -SiC samples even when all the other processing conditions were kept the same.



Fig. 8. The BE-SEM pictures of ZrB_2 -SiC—10 vol% WC sintered at 2000°C (a) and 2200°C (b). Note the different morphologies of the brightest phase (W, Zr)_{ss}B in the two images: rounded at 2000°C, and irregular shaped at 2200°C, typical of crystallization from a liquid phase.



Fig. 9. Typical microstructures of $(W, Zr)_{ss}B$ (a, d, i) and $(W, Zr)_{ss}Si_2$ (b, c). (e)(g) showed that ZrB_2 grains were wetted by $(W, Zr)_{ss}B$. Example of a WB/ZrB_2 interface showing a clean grain boundary (h). Insets in (a) and (i) are the electron diffraction of ZrC and faceted ZrB_2 grain.

(ii) The aspect ratio of the ZrB_2 grains could be tailored by the sintering temperature or the WC addition. The increasing WC amount accelerates the anisotropic grain growth of ZrB_2 .

When grains are immersed in a liquid phase for enough time, which is in the chemical equilibrium with the grains, the shape of the grain as well as its crystallographic orientations can be determined by Wulffs rules. It can be described by the following reaction²⁵:

$$\gamma_1/h_1 = \gamma_2/h_2 = \gamma_i/h_i \tag{6}$$

where, h_i represents the distance perpendicular from the crystal center to the plane and γ_i is the specific interfacial energy of the crystallographic plane *i*.

 ZrB_2 has a hexagonal crystal structure (*P6/mmm*), benefiting from this point, its interface free energy is anisotropic. Based on Wulffs rules and the above observations, it is natural to consider that the reasons for the elongation of ZrB_2 grains could be that: (1) liquid phase(s) was formed in ZrB_2 -SiC–WC and the liquid phase must be associated with WC additions and temperature; (2) the liquid phase(s) could well wet the matrix, so the matter transfer process between the matrix and the liquid can easily occur. Some evidence concerning the above assumptions was considered as below.

(4) Possible Liquid Phases at $2200^{\circ}C$

Besides SiC and ZrB₂, the sintered ceramic composite contains amounts of (W, Zr)_{ss}Si₂, (W, Zr)_{ss}B, and (Zr, W)_{ss}C. The melting point (T_m) of WSi₂ is 2150 °C, the T_m of Zr is only 1920°C, and we are not aware of any ternary compound existing in the W–Si–Zr system was reported. For subternary system WSi₂–Si– Zr (along Si–Zr side and at Si corner in the W–Si–Zr system), it is possible to form two pseudo-binary systems WSi₂–Si₄Zr₅ and WSi₂–Zr (all with melting points) in case of no intermediate compounds was formed. According to the principle of phase diagram topology, addition of Zr into WSi₂ will lower its melting temperature as liquidus line shifting away from $T_m =$ 2160°C. As such, the melting points of corresponding solid solution of (W, Zr)Si₂ will be below 2160°C. Thus, it must be molten at the sintering temperature (2200°C).

The measured $T_{\rm m}$ of (Zr, W)_{ss}C is as high as 2900°C.²⁶ Thus, the task here is to verify the existence of liquid (W, Zr)_{ss}B phase at or below the sintering temperature, for no literatures mentioned its eutectic point. It is interesting that the microstructure features of ZSW sintered at 2000° and 2200°C, especially the distributions of (Zr, W)_{ss}C and (W, Zr)_{ss}B phases are quite different.

At 2000°C, as supported by reaction (5), $(Zr, W)_{ss}C$ and $(W, Zr)_{ss}B$ usually appeared in the same region, at ZrB_2/ZrB_2 or



Fig. 10. The bright field image (a) and high-angle annular dark-field imaging (HADDF, b) of elongated ZrB_2 grains. The line scan (dotted in (b)) of W content and the spot analysis (circled in b) of the molar ratio between W and Zr are shown in (c) and (d), respectively.

 ZrB_2 /SiC grain boundaries, adjacent to each other (as arrowed in Fig. 8(a)). Nevertheless, the regions rich in (Zr, W)_{ss}C are poor in (W, Zr)_{ss}B, when the sintering temperature increases to 2200°C (Fig. 8(b)). Such grain arrangement and movement were nearly impossible to be completed in a solid state sintering process due to the limited diffusion. A direct evidence for the liquid phase of (W, Zr)_{ss}B is described in Fig. 9(a). Small (Zr, W)_{ss}C grain was found to be immersed in (W, Zr)_{ss}B grain, strongly supporting the melting of (W, Zr)_{ss}B that occurred during this stage.

(5) ZrB₂ Grains Evolution in the Liquids

The existence of $(W, Zr)_{ss}Si_2$ grains was scarce in all the asobserved areas. Among the $(W, Zr)_{ss}Si_2$ grains, there are only two different configurations. One is located near the SiC grains (Fig. 9(b)), indicating that the formation of $(W, Zr)_{ss}Si_2$ should be related to SiC and the following diffusion of Zr (from ZrB₂ or ZrC) into WSi₂. Another configuration has been found at the triple junction point (Fig. 9(c)). To segregate all the silicides into the triple points by single solid diffusion is very unlikely without the help of capillary force induced by means of liquid, again, and the microstructure observed above strongly suggests (W, Zr)_{ss}Si₂ to be a liquid phase that appeared in the matrix.

However, when such kind of liquid phase was used to explain the elongation of ZrB_2 grains, some arguments against this hypothesis are raised.

First, one of the most probable way for the formation of $(W, Zr)_{ss}Si_2$ relied on the reaction between SiC and W. Large amount of SiC exists in the matrix, whereas W from the reaction between ZrO₂ and WC is substantially limited. Based on

reaction (1) and ZrO_2 content, 5 vol% WC is enough to consume all the ZrO_2 . Thus, though the addition of WC increased from 5 to 10 vol%, the resultant amount of (W, $Zr)_{ss}Si_2$ was unchanged. It could not explain the anisotropic grain growth of ZrB_2 accelerated at the same time. Second, the observed (W, $Zr)_{ss}Si_2$ was limited and ZrB_2 grains were not well wetted by it according to the relatively large dihedral angles in the range from 30° to 60° measured in their solid/liquid grain boundaries.

Compared with (W, Zr)_{ss}Si₂, the appearance of (W, Zr)_{ss}Brelated liquid phase was more reasonable to explain the formation of plate-like ZrB₂, as discussed below:

(i) Wetting or dewetting of grain boundary. Some detailed microstructures of (W, Zr)_{ss}B, obtained from ZSW10 are shown in Figs. 9(a), (d)–(g). Most of their interfaces are flat sintered at 2000°C (Fig. 9(d)), while curved with concaveness toward itself when the sintering temperature was elevated to 2200°C (Figs. 9(a), (e)–(g)). This suggests a tendency of (W, Zr)_{ss}B from dewetting (Fig. 9(d)) to wetting of grain boundaries (Figs. 9(a), (e)–(g)), which favored in the elongation of ZrB₂ grains at the same time. Furthermore, clean grain boundary between (W, Zr)_{ss}B and ZrB₂ was observed (Fig. 9(h)).

(ii) The solubility and matter transfer process between the liquid phase and the matrix.

Some W and Zr were incorporated into ZrB_2 and WB, as confirmed by Fig. 1. It demonstrated that ZrB_2 and the liquid phase were mutually soluble. Another direct evidence for such matter transfer process was the inhomogeneous distribution of W in elongated ZrB_2 grains. Figs. 10(a) and (b) are the bright field images and high-annular angle dark-field images (HADDF) at the same region. HADDF is highly sensitive to variations in the atomic number of atoms in the sample. By using of it, it is easy to distinguish the phases of $(W, Zr)_{ss}B$ and (W, $Zr)_{ss}Si_2$ (A' and B' as arrowed in Fig. 10(b)), while nearly no contrast difference could be observed from their corresponding bright field images (A and B as arrowed in Fig. 10(a)). Furthermore, both of the line scan (W) result (Fig. 10(c)) and the spot analysis (the molar ratio of W and Zr, Fig. 10(d)) show a composition change of W in ZrB2 grains was existed, normally lower in the center and higher near the edge. So, the matter transfer process indeed existed in these two phases as confirmed by the process of cations interdiffusion.

(6) Overall Mechanisms

The necessary and sufficient conditions for Ostwald ripening by liquid phase sintering are: (1) an abundant liquid phase has to be present in the matrix at the sintering temperature; (2) the matrix has to be soluble enough in the liquid; (3) liquid has to be wet the grain boundary of the matrix well. All of these are satisfied in this system according to the above discussions, strongly confirming the liquid phase sintering mechanism. Namely, in the sintering process of ZrB₂-SiC-WC at 2200°C, small particles dissolved in the liquid were transported through the liquid phase and then precipitated on large particles.

During this process, the most possible mechanisms for the anisotropic grain growth of ZrB₂ should include the following steps. WB was firstly formed by reaction (5) at about 1450°C. As the temperature increased, WB could "absorb" the impurities M (M = O and other metallic impurities) in the matrix or "accept"interdiffusion cations from ZrB2 grains and form liquid phases based on W-Zr-B-M. Such liquid phase can well wet ZrB₂ grain boundaries (Figs. 10(e)–(g), and it accelerates the matter transfer process. Under the external driving force induced by capillary force, the grains under average size were dissolved in the liquid. After a long enough period, liquid was chemically in equilibrium with ZrB₂ grains. In case the equilibrium state was disturbed, partial atoms of Zr and B in the liquid were reprecipitated on ZrB₂ grains based on the minimum interfacial energy principle and Wulffs rules. The evidence for such phenomenon is the sharp composition of W at the edge of ZrB₂ grains (Figs. 10(c) and (d)). The main matter transfer route has been shown in Fig. 9(i), which comes from the ZrB₂ grain with rough surface to adjacent faceted ZrB_2 platelet, by means of W-Zr-B-M liquid phase through dissolution-transportation-precipitation process.

Conclusions

The following conclusions are obtained based on the microstructure analysis and thermodynamic calculations in this work:

(1) The actual morphology of ZrB_2 grains in ZrB_2 -SiC-WC sintered at 2200°C was platelets with preferential growth direction normal to c-axis, and the aspect ratios could be further tailored by the WC amount.

(2) Thermodynamic predictions and XRD analysis confirmed the two independent chemical reaction routes for removing ZrO_2 in the current material system. One is the reduction of ZrO₂ by single WC, and another one is the reaction in ZrO₂-WC-ZrB₂. Here, ZrO₂ plays an important role on the reaction process, for it can decrease the favorable reaction temperature between WC and ZrB₂, from 2300° to 1234°C.

(3) The densification of ZrB2-SiC doped by WC was enhanced by means of liquid phase formation. Liquid phase could be either (W, Zr)_{ss}B or (W, Zr)_{ss}Si₂. When (W, Zr)_{ss}B was considered as the effective liquid phase, all the conditions for Ostwald ripening of ZrB₂ grains were satisfied. Once again, the TEM demonstrated to be a necessary tool for the investigation of ZrB₂-based ceramics. By this technique it was possible to identify the sources and the composition of the liquid phases and it to advance plausible hypotheses on the driving force which led to the anisotropic grain growth of ZrB₂ grains.

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