TEM investigation of hot pressed -10 vol.%SiC–ZrB₂ composite

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The polypyrism of SiC, phase transformation of ZrB₂ and the interfaces between SiC and ZrB₂ were investigated using high resolution TEM in a hot pressed 10 vol.%SiC-ZrB₂ composite. In most cases, no grain boundary interphases between hexagonal ZrB₂ and 6H-SiC phases were observed with SiC being both inter- and intragranular. Occasionally, 6H-SiC transformed into 3C and 15R and hexagonal ZrB₂ transformed into cubic ZrB. High resolution TEM showed no grain boundary interphases in most regions. Energy dispersive X-ray spectroscopy and electron energy-loss spectroscopy analyses showed the presence of oxygen throughout the sample. The phase transformation of SiC and ZrB₂, and the interphase formation between SiC and ZrB₂ grains are discussed.

Keywords: UHTC's, Interphases, Dislocations, ZrB₂, SiC, Microstructure

Introduction

The cornerstone of ultrahigh temperature ceramics (UHTC) is a small group of diboride and carbide ceramic–matrix composites including ZrB₂–SiC, HfB₂–SiC, ZrC–SiC, HfC–SiC, and ZrB₂–SiC–C. They have a unique set of material properties including unusually high thermal conductivity that makes them particularly well suited for sharp body applications in hypersonic flows. However, their use has been limited due to poor fracture toughness, moderate thermal shock and oxidation behaviour and inability to make them fully dense. Previous evaluation of these materials suggested that their poor properties were due to agglomerates, inhomogeneities and grain boundary impurities, all of which were believed to be associated with ceramic processing problems.

Among UHTCs, ZrB₂ has the lowest theoretical density (6.09 g cm⁻³), which makes it attractive for aerospace applications. Its high melting temperature, good thermal shock and oxidation resistance and relatively low cost when compared with HfB₂ based ceramics make it more attractive than other non-oxide structural ceramics. Often, SiC is added to ZrB₂ to enhance its oxidation resistance and limit grain growth during densification. Additions of up to 30 vol.%SiC particulates have been found to improve the four-point bend strength of ZrB₂ from ~565 to ~1089 MPa and fracture toughness from 3.5 to 5.25 MPa m⁰.² by limiting grain growth and promoting crack deflection.

In recent years, significant progress has been made in densification and characterisation of Zr and Hf based UHTCs. Surprisingly, few reports appear in the literature of microstructural defects in grains or at interfaces using transmission electron microscopy (TEM). Therefore, in this paper we report an investigation of phase transformations of SiC and ZrB₂ and the interphase formation between ZrB₂ and SiC in 10 vol.%SiC–ZrB₂ composites sintered by hot pressing.

Experimental

Materials and methods

ZrB₂ powder (~98.5%, dₐ=2 μm, 0-2% C, 0-9%O, 0-2%Hf, grade B; HC Starck, Newton, MA, USA) and SiC powder (x-SiC, 98.5%, dₐ=0.7 μm, grade UF-10; HC Starck) were used as the starting materials. Phase analysis by X-ray diffraction (XRD) and using selected area electron diffraction (SAED) patterns confirm that both ZrB₂ and SiC have a hexagonal structure with lattice parameters of a=3.17 Å, c=3.53 Å and a=3.08 Å, c=15.12 Å respectively. To reduce particle size and promote intimate mixing, batches of composition 90 vol.%ZrB₂ and 10 vol.%SiC were attrition milled (model 01-HD; Union Process, Akron, OH, USA). Milled powders were hot pressed (model HP-3060; Thermal Technology, Santa Rosa, CA, USA) into graphite dies lined with graphite foil and coated with BN. The hot press furnace was heated at an average rate of ~5°C min⁻¹ to 1900°C at ~17°C min⁻¹ with simultaneous application of 32 MPa load in flowing argon. After 45 min the sample was cooled at...
~20°C min−1 to room temperature. Each billet is 
~40 mm in diameter and ~5 mm in thickness. More
details of the hot pressing procedure are given by 
Zimmermann et al. 39

**Characterisation by TEM**

Specimens for TEM observation were prepared from hot pressed materials using conventional mechanical polishing and ion thinning. The ion thinning was performed using a Gatan model 691 precision ion polishing system. Bright field (BF) images and SAED patterns were acquired using a JEOL JEM-2000EX electron microscope operating at 200 kV. The Burgers vectors \( \mathbf{b} \) of dislocations were determined using the relation \( \mathbf{g} \mathbf{b} = 0 \), where \( \mathbf{g} \) is the diffraction vector. High resolution TEM (HRTEM), energy dispersive X-ray spectroscopy (EDS) and electron energy loss spectroscopy (EELS) were carried out using an FEI Titan 80–300 scanning transmission electron microscope operating at 300 kV.

**Results and discussion**

Figure 1 shows typical BF images of the morphologies of different phases and the interfaces in the composites. Figure 1a clearly reveals small (0–4 μm), intragranular spheroidal SiC grains within (about 2–3 μm sized) ZrB2 grains containing dislocations some of which appear to be associated with the intragranular SiC. Figure 1b reveals an intergranular SiC at a ZrB2 triple junction. The inset SAED pattern is a [11–20] zone axis revealing that the SiC is the 6H polytype. ZrB2 is often observed to have a hexagonal symmetry. The dislocations observed in ZrB2 around SiC in Fig. 1a are most likely caused by thermal expansion mismatch between ZrB2 (P63/mmc) (Ref. 41) and SiC (P63mc) (Ref. 42) grains. Figure 1c–d shows bright field images of a ZrB2 grain in direct contact with a SiC grain. Diffraction contrast imaging of the dislocations in ZrB2 has been performed under two-beam conditions using different diffraction vectors (\( \mathbf{g} = 0001 \) and \( \mathbf{g} = 10\overline{1}0 \)). Arrows indicate the direction of \( \mathbf{g} \). Dislocations are observed to originate at the grain boundary interfaces. The dislocation Burgers vectors are determined to be either \( \mathbf{a} = \frac{1}{3}(11\overline{2}0) \) in Fig. 1c or \( \mathbf{c} = (0001) \) in Fig. 1d using \( \mathbf{g} \mathbf{b} \) criteria. Figure 1e shows a BF image of ZrB2–SiC composite. The grain with striated contrast is SiC. The inset in Fig. 1e shows the [110] zone axis SAED pattern taken from the circled area, which can be indexed as \( \beta \)-SiC with a zinc blende structure (3C-SiC). The characteristic
double diffraction spots and streaks in the SAED pattern reveal the presence of twins and stacking faults, respectively.\textsuperscript{43–45} No appreciable grain growth occurred during hot pressing as SiC and ZrB\textsubscript{2} grain sizes remain the same as those of the initial particles.

Grains with similar features are observed throughout the microstructure. Figure 2\textit{a} shows a typical BF image of a ZrB\textsubscript{2}/SiC interface. Analysis using EELS (Figs. 2\textit{b} and \textit{c}) confirms the striped region A is SiC while region B is ZrB\textsubscript{2}. Figure 2\textit{e} shows an HRTEM image taken down the [11\textsubscript{2}0] zone axis from the area F in the SiC grain. The SAED pattern obtained from this grain (Fig. 2\textit{e}) can only be indexed as 15R-SiC. Careful examination of the SAED pattern reveals streaks between the diffraction spots, which indicate the presence of stacking faults in the 15R-SiC. The HRTEM image reveals a superlattice structure with \(c\) parameter fifteen times that of the 3C-SiC polymorph. The lattice parameters of 15R-SiC are determined to be \(a=3.06\ \text{Å}\) and \(c=37.07\ \text{Å}\). As can be seen from Fig. 2\textit{d} the ideal structure of 15R-SiC has an ‘ABCACBCABACABCA’ or (3\textsuperscript{-}2\textsuperscript{3}) sequence.

Figure 2\textit{f} shows a HRTEM image at the [0001] zone axis taken from the area G in the ZrB\textsubscript{2} grain. The inset shows the corresponding SAED pattern which can be indexed using the lattice parameters of hexagonal ZrB\textsubscript{2}. The planar spacings for \{10\textsubscript{1}0\} are measured to be 3.17 \text{Å} which matches that of hexagonal ZrB\textsubscript{2}. Thus, the chemical composition, SAED pattern and the HRTEM image of region B confirm that it is hexagonal ZrB\textsubscript{2} which has undergone no phase transformation on processing. SiC is commonly observed in this composite: intragranular (Fig. 1\textit{a}), intergranular (Fig. 1\textit{b}) and with faulted contrast (Figs. 1\textit{e} and 2\textit{a}). The striped features in
the SiC grain are attributed to planar defects such as twins and stacking faults.

High resolution TEM was performed to clarify the nature of the grain boundary between SiC and ZrB$_2$ in Fig. 2a. Figure 2g shows the HRTEM image taken from area C in Fig. 2a around the interface. Figure 2g shows an atomically flat and coherent interface between SiC and ZrB$_2$. It is observed that the grain boundary is clean and does not contain any secondary phases. Furthermore, the region of A in Fig. 2a closer to the SiC/ZrB$_2$ interface shown as 3C in Fig. 2g reveals a 2-49 Å lattice spacing and the atomic arrangements show cubic structure. The lattice parameter is calculated to be a = 4-32 Å from the HRTEM image. Since EELS analysis confirms the presence of only Si and C. This region is confirmed as 3C, i.e., β SiC (a = 4-35 Å). The slightly smaller lattice parameter may be caused by the strain around the interface.

Figure 2g shows two distinct interfaces between 15R-SiC and 3C-SiC, 3C-SiC and hexagonal ZrB$_2$. The crystallographic orientation relationships between these interfaces were determined from Fig. 2g. The crystallographic orientation relationship between 15R- and 3C-SiC is [1120][110] and (0001)[011]. However, the crystallographic orientation relationship between 3C-SiC and ZrB$_2$ is [1100][0001] and [111][010]. In this orientation, the (0100) planes of the hexagonal structure (ZrB$_2$) and the (111) planes of the cubic structure (3C-SiC) have minimal misfit and the strain can be accommodated more easily. The crystallographic orientation relationships of [1120][110] and (0001)[011] are commonly observed for interfaces between a hexagonal and cubic phases.

Figure 3 shows an HRTEM image of a ZrB$_2$/ZrB$_2$ interface in the ZrB$_2$-SiC composite. Grain 2 can be tilted to [011] zone axis perpendicular to (-2 -4 -25) plane, while grain 1 cannot be tilted to a low index zone axis. This means that there is no preferential orientation relationship between these two grains. A closer look at the HRTEM image of the ZrB$_2$/ZrB$_2$ interface reveals that no secondary glassy or crystalline interphases are present.

Figure 4a shows an HRTEM image of a further interface in the ZrB$_2$-SiC composite. Both grains 1 and 2 can be tilted to respective zone axes which indicates that they have crystallographic orientation relation between them. Although EDS analyses (Fig. 4b) reveal the presence of Zr and B in both grains, quantification of EDS spectra indicates that the composition of these two grains is different. In grain 1 the atomic ratio of Zr/B is close to 1:2, while in grain 2 the atomic ratio of Zr/B is close to 1:1. Selected area electron diffraction and HRTEM also confirm the phase differences. Figure 4c shows an enlarged HRTEM image of grain 2. The atomic arrangement clearly reveals it to be a cubic structure with a plane spacing of 2-69 Å for the [111] plane. As ZrB$_2$ is only known to exist in cubic form, the existence of ZrB$_2$ is unlikely and also the planar spacing of grain 2 does not match any of the SiC polytypes. In addition, the SAED pattern taken from grain 2 (not shown) can be indexed using a lattice parameter of a cubic phase (4-65 Å). As zirconium boride has another two cubic phases ZrB$_4$ (a = 4-65 Å) and ZrB$_{12}$ (a = 7-40 Å), taking into account the EDS quantification results, lattice parameter, and the crystal structure, grain 2 is most likely to be cubic ZrB. This observation suggests that a small amount (perhaps ~1 vol%5) hexagonal ZrB$_2$ transforms into cubic ZrB during the hot pressing.

Figure 5 shows a typical BF and HRTEM image of a three-grain junction having two interfaces. Grains C and B in Figure 5a have similar contrast while grain A has slightly darker contrast. Grain A occurs as an intergranular phase between the two large grains. Analysis using EDS confirms that the small grain is SiC and the larger grains are ZrB$_2$. Selected area electron diffraction of the large grains reveals that the ZrB$_2$ grains are hexagonal while SAED of the small grain reveals it as 3C-SiC. Figure 5b shows an HRTEM image of the interface between grain A and grain B revealing a thin 3–6 nm amorphous layer. Analysis of this interphase using EDS reveals Si and O, suggesting an amorphous silica layer forms the interphase at the grain boundary. Although XRD did not detect the presence of oxides or any other secondary phases, EDS and EELS analyses always show the presence of oxygen throughout the sample. The presence of oxygen in the sintered samples is due to its presence in the starting materials.

In this study, uncharacteristic SiC features have been observed including the transformation from α (6H) to β
(3C) polytypes. The more usual transformation is β- to α-SiC which is thermodynamically not reversible. Only Kieffer et al. have observed 6H- to 3C-SiC transformation in microcrystalline powder at 2800 K when annealed for 4 h in vacuum. An ab initio study on the polytypic transformation suggests that a dislocation mechanism may be responsible for the temperature and deformation induced transitions. Calculated energy barriers for 6H→3C make the dislocation mechanism highly favourable for polytypic transformations in SiC. The dislocation based polytypic transformation results from the strength of the compression applied to 6H during hot pressing. In addition, other impurities such as carbon, silicon or oxygen stabilise the 3C-SiC structure.

Another interesting feature is the transformation of ZrB₂ into ZrB. Champion et al. studied the Zr/ZrB interface and observed ZrB as the grain boundary interphase. Electron diffraction also showed the existence of ZrB cubic phase at the metal/ceramic interface and in some ZrB₂ grains. The proposed phase diagram also suggested a peritectoid transformation.
**Conclusions**

High resolution TEM observations reveal that $6H$ $z$-$\text{SiC}$ transforms into $3C$ $\beta$- and $15R$-$\text{SiC}$ and hexagonal $\text{ZrB}_2$ transforms into cubic $\text{ZrB}$ in some regions of the hot pressed $\text{ZrB}_2$–$\text{SiC}$ composites. Although these newly formed phases during hot pressing are only present in small amounts, they can significantly influence the high temperature mechanical properties and oxidation behaviour of the composites. The Burgers vectors of the observed dislocations in $\text{ZrB}_2$ are determined to be either $a/2\langle 1120 \rangle$ or $c\langle 0001 \rangle$ using $gb$ criteria. The observations at interfaces revealed that there are no grain boundary phases.

**Acknowledgements**

One of the authors, DJD thanks the Defence Science and Technology Laboratory (Dstl) for providing the financial support for this work under contract number DSTLX-1000015413. The authors kindly acknowledge use of the FEI TITAN 80–300 STEM facility at Imperial College London for HRTEM characterisation of interfaces.

**References**


