In-situ observation of oxidation behavior in ZrB$_2$–SiC–ZrC ternary composites up to 1500°C using high-temperature observation system

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ZrB$_2$–SiC–ZrC (ZSZ) ternary composites of four differing compositions were fabricated by spark plasma sintering (SPS). The effect of the ZrB$_2$/ZrC ratio on the oxidation behavior was examined by thermogravimetric (TG) analysis and microstructural observations. In addition, in-situ observation above 1500°C was performed using a high-temperature observation system (HTOS). ZSZ composites with high ZrC contents were fully oxidized at temperatures below 1500°C. However, ZS composites with low ZrC contents formed protective oxide layers during heat exposure. These layers protected the unreacted regions from further oxidation. Island nucleation was successfully observed on the surface oxide layer at 1500°C using the HTOS. The nucleation of islands strongly depended on the ZSZ composition. The difference in oxidation behavior originated from the concentration and interparticle distance of the ZrC in the as-sintered compacts.

Key-words : Ultra-high temperature ceramics (UHTCs), ZrB$_2$, Oxidation, In-situ observation

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1. Introduction

Ultra-high temperature ceramics (UHTCs) are defined as transition metal diborides, carbides, and nitrides with melting points exceeding 3000°C. UHTCs and composites containing them can be applied in the thermal protection systems (TPS) of atmospheric re-entry aerospace vehicles.1−5 The UHTC of ZrB$_2$ has an especially low density (5−6 g/cm$^3$), high Young’s modulus (~50 GPa), and high toughness (~5 MPa$m^{1/2}$).6,7 However, ZrB$_2$ is rapidly oxidized at temperatures exceeding 1200°C in air.8,9 In order to improve the oxidation resistance of ZrB$_2$, material systems including ZrB$_2$–SiC, ZrB$_2$–MoSi$_2$, and ZrB$_2$–SiC–AlN have been proposed.10,11 Among these systems, ZrB$_2$–SiC binary UHTC composites have received significant research focus because they are tougher than monolithic ZrB$_2$ ceramics and show good oxidation resistance, even above ~1200°C, because of the formation of a surface SiO$_2$ layer by the oxidation of SiC. Beneath the SiO$_2$ glassy oxide layer, SiC reacts with oxygen to form gaseous SiO above 1500°C, evolving a porous layer during oxidation.12,13

Further improvements in the oxidation resistance of ZrB$_2$–SiC have been achieved. Some researchers have added transition metals or rare-earth borides, carbides, nitrides, oxides, and/or silicides, such as TaB$_2$, WC, ZrN, La$_2$O$_3$, and ZrSi$_2$, to ZrB$_2$–SiC to improve the oxidation resistance of the binary composite.14−17 ZrC is an especially effective additive in ZrB$_2$–SiC because high volume expansion occurs during the oxidative transition from ZrC to ZrO$_2$.18,19 The quantity of expansion during this oxidation is approximately twice that during the oxidation of ZrB$_2$ to ZrO$_2$.18,19 Compared to ZrB$_2$–SiC and ZrB$_2$–ZrC composites, ZrB$_2$–SiC–ZrC ternary composites (hereafter denoted as ZSZ) have finer grain sizes because grain growth of ZrB$_2$ during sintering is suppressed.20 Wang et al. oxidized ZrB$_2$–20 vol% SiC–6 vol% ZrC at ~1760°C and demonstrated that the protective oxide layer on the product was composed of SiO$_2$ and ZrO$_2$.21 They also revealed that the oxidation kinetics at ~1760°C for 900 s obeyed a parabolic law, which verified the formation of a protective oxide layer on the surface during oxidation. Akin et al. fabricated ZSZ composites with four different compositions: ZrB$_2$–10 vol% SiC with 30 and 40 vol% ZrC, and ZrB$_2$–20 vol% SiC with 20 and 30 vol% ZrC. They conducted oxidation tests at 1400–1600°C for 180 min and concluded that all ZSZ composites formed protective oxide layers during oxidation; however, high amounts of ZrC of 30 vol% or greater caused aggressive oxidation.22 Recently, Liu et al. oxidized ZrB$_2$–20 vol% SiC (ZS20), ZrB$_2$–20 vol% SiC–10 vol% ZrC (ZS20Z10), and ZrB$_2$–20 vol% SiC–20 vol% ZrC (ZS20Z20) at temperatures reaching 1600°C for 0−4 h and reported that the mass gain after oxidation for 4 h by ZS20Z20 (~55 mg/cm$^2$) was much larger than that of ZS20 and ZS20Z10 (~10 mg/cm$^2$ and ~20 mg/cm$^2$, respectively).15 They concluded that ZrC dominated the progress of oxidation for ZSZ composites.23 The addition of ZrC is expected to improve the porous layer structure by the ~32% volume expansion in the transition from ZrC to ZrO$_2$.12,13,15 However, this expansion also causes drastic material consumption during oxidation. Thus, the optimal ZrC content has not yet been identified.

In order to optimize the ZrC content, a thorough understanding of the effect of ZrC content on the oxidation behavior of ZSZ composites is needed. The oxidation behavior of ZSZ composites has been investigated by conventional thermogravimetric (TG) analyses and microstructural observations using post-tested

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specimens. In addition, in-situ monitoring during heating could provide important information regarding the oxidation of ZSZ composites, because the microstructure of the sample evolves as time proceeds. Surface observation at temperatures above 600°C is difficult because the intensity of visible light radiating from the heated sample disturbs observation. Recently, Gangireddy et al. developed an optical system equipped with an electric heating system to observe the rapid oxidation behavior of ZrB$_2$–SiC binary composites. They observed that a protective oxide layer was formed on the ZrB$_2$–SiC by oxidation above 1450°C. At this temperature, they observed crystalline ZrO$_2$, which was gradually formed by the oxidation of ZrB$_2$, and a glassy layer formed by SiC oxidation. They reported the simultaneous dynamic phenomenon of the evolution of islands formed by CO gas during the oxidation of SiC. Thus, an in-situ observation system usable at high temperatures is effective for gaining further understanding of the dynamic oxidation of ZrB$_2$–SiC binary composites.

The objective of this study is to determine the optimal content of ZrC for ZSZ composites. We apply a newly developed high-temperature observation system (hereafter denoted as HTOS) to the understanding of the oxidation mechanism of ZSZ composites with different ZrC contents up to ~1500°C. For comparison purposes, conventional experiments are also performed by TG and microstructural analysis. Furthermore, the microstructural evolution of each specimen during oxidation exposure testing is examined using an in-situ observation system. Based on the results of these experiments, the effect of ZrC content on the oxidation behavior of ZSZ composites is discussed.

2. Experimental procedure
2.1 Sample preparation
The starting particles used in this study were ZrB$_2$ (Grade-F, average particle diameter ~2 μm, Japan New Metals Corp., Tokyo, Japan), α-SiC (Grade UF-15, average particle diameter ~0.5 μm, H.C. Starck GmbH, Berlin, Germany), and ZrC (Grade-F, average particle diameter ~2 μm, Japan New Metals Corp., Tokyo, Japan). Four powder mixtures were designed, with compositions summarized in Table 1. The powder mixtures were milled using a SiC ball of 10 mm in diameter, jar, and milling media (P6, FRITSCH GmbH, Rudolstadt, Germany) for 24 h. After drying, the powders were sieved through a metallic sieve with a 125-mesh screen size and placed in a carbon die of 15 mm in diameter and 3 mm in thickness. The compacts were formed by SPS (SPS-520S, Fuji Electronic Industrial Co., Ltd., Saitama, Japan). For all compositions, sintering was performed in an Ar atmosphere at 1950°C under a uniaxial pressure of 50 MPa and a holding time at the maximum temperature was set to 2 min. The as-fabricated disk-shaped specimens were polished using diamond paste with particles of up to 1 μm in size. The apparent density of each specimen was measured by the Archimedes method.

The polished surfaces were observed using a field-emission scanning electron microscope (FE-SEM, S-4200, Hitachi High-technological Corp., Tokyo, Japan).

2.2 TGA studies for ZSZ composites
TG analysis was performed for each composition, using a rectangular sample with the dimensions of 0.8 × 0.3 × 3 mm. The sample was placed into an alumina crucible of 5.2 mm in diameter and 2.1 mm in depth. The test was performed in a TGA furnace (TG–DTA 2020SA, Bruker AXS GmbH, Karlsruhe, Germany). Alumina powder was used for calibration. Testing was performed from 23 to 1500°C with a temperature increase rate of 10°C/min under an air gas flow (100 mL/min). The post-oxidized bulk specimens were characterized by X-ray diffraction (XRD, RINT-Ultima III, Rigaku Corp., Tokyo, Japan) using a Cu Kα X-ray source. The diffraction measurement was performed with a step rate of 2.0 degree/min and a diffraction angle range 2θ of 20 to 80 degrees. Elemental analysis was done by energy-dispersive X-ray spectroscopy (EDS, AMETEC Inc., Mahwah, NJ, USA) and post-oxidation observation of cross-sections of the ZSZ composites was performed by FE-SEM.

2.3 In-situ observation of oxidizing ZSZ composites by HTOS
In-situ observation was performed using an HTOS as reported in the literature. Fig. 1 shows a schematic of the HTOS. The system consists of a UV charge-coupled device (CCD) camera with a maximum resolution of 1004 × 1002 pixels (BU-56EMU, BITRAN, Saitama, Japan). The CCD is sensitive to light of 200 to 1010 nm in wavelength. An objective lens with a long working distance (VH-Z50L, Keyence Corp., Osaka, Japan) was used for in-situ observation to reduce the heat damage to the system. The UV light source, generated by a mercury lamp (USH-500SC2, Ushio Inc., Tokyo, Japan) with a pressure range of 0.5 to 5 MPa, was introduced to the lens through an optical fiber. A light-pass

![Fig. 1. Schematic of high-temperature observation system (HTOS) used in this study.](Image 340x196 to 510x348)

Table 1. Composition and density of sintered compacts fabricated in this study

| Composition (vol%) | Density |
|-------------------|---------|
| ZrB$_2$ | SiC | ZrC | Theoretical density, $\rho_t$ (g/cm$^3$) | Apparent density, $\rho_a$ (g/cm$^3$) | Relative density (%) |
| ZrB$_2$–SiC–ZrC (ZSZ-1) | 20 | 16 | 64 | 6 | 5.68 | 94.7 |
| ZrB$_2$–SiC–ZrC (ZSZ-2) | 34 | 16 | 50 | 5.92 | 5.62 | 94.9 |
| ZrB$_2$–SiC–ZrC (ZSZ-3) | 50 | 16 | 34 | 5.82 | 5.54 | 95.2 |
| ZrB$_2$–SiC–ZrC (ZSZ-4) | 64 | 16 | 20 | 5.74 | 5.44 | 94.8 |
filter (U340-25, Hoya Candeo Optronics Corp., Saitama, Japan) was inserted between the CCD camera and objective lens to remove the effects of thermal radiation from the sample. Oxidation exposure testing was performed using an infrared (IR) image furnace (IR-QP2-4S, Yonekura Manufacturing Co., Ltd., Yokohama, Japan).

Square samples (1.5 × 1.5 × 1 mm) of the ZSZ composites were used for in-situ observation. In the present study, the observed area was approximately 2 mm². Before the oxidation exposure test, Vickers impressions were marked on the surfaces of the specimens with an applied load of 98.1 N. For testing, the specimen was affixed to an alumina base plate and heated in dry air up to 1500°C at the heating rate of 100°C/min. During the test, the temperature history was recorded by an R-type thermocouple. Digital images were captured at intervals of 30 ms.

3. Results & discussion

3.1 Morphology of as-sintered ZSZ composites
Table 1 shows the theoretical, apparent, and relative densities of each specimen. The relative densities of all specimens approach 95%. Figure 2(a) shows the typical microstructures of the as-fabricated ZSZ composites. The dark, bright, and intermediate contrast regions correspond to SiC, ZrC, and ZrB₂, respectively. ZrC particles are connected continuously in the sintered compacts of ZSZ-1 and 2. On the other hand, the average distance between ZrC particles is 2–3 μm in ZSZ-3 and 4. SiC particles are dispersed uniformly in all compacts. Figure 2(b) indicates the distribution of particle sizes in the as-sintered compacts. The size distributions of SiC and ZrC particles are within 0.5–4 μm and are nearly identical for all compositions. However, the 1–7 μm particle size of ZrB₂ in ZSZ-4 is larger than that in the others.

In the sintering of UHTC composites, it is necessary to determine the optimal sintering conditions for the desired compositions to prevent poor sintering or particle coarsening.6),8),10),12) However, in this study, ZSZ composites of four different compositions were sintered under equivalent conditions and all sintered compacts reached relative densities of 95%. The sintering conditions for the ZSZ composites in this study are higher in temperature and shorter in holding time compared to those in some studies.8)–10) Because ZrC has the highest melting point of the compounds in the starting powders, the higher temperature accelerates the sintering of ZrC.24) Meanwhile, the shorter holding time probably suppresses the coarsening of ZrB₂ powder.25) In the present study, the particle size clearly increases from those of the starting powders during sintering for ZSZ-4; this is attributed to the coarsening of ZrB₂ particles. However, the relative density of the ZSZ-4 compact is similar to that of the others. Thus, the sintering conditions used in this study are probably optimal for the sintering of ZSZ composites containing 20–64 vol% ZrB₂ or ZrC.

3.2 TG analysis and microstructural observation
The relationships between weight changes and temperature increase during oxidation are shown in Fig. 3(a), with a magnification depicted in the inset Fig. 3(b). Each specimen begins to increase in weight at 600°C; however, the slope of the curve strongly depends on the specimen composition. For ZSZ-1, weight gain becomes rapid at 700°C but slows above 900°C. Weight loss begins above 1200°C. For ZSZ-2, 3, and 4, although the values of weight gain differ among the specimens, the weights increase at 600°C and remain constant between 800 and 1100°C. Above 1200°C, each specimen begins a slight increase in weight.

XRD patterns for the ZSZ composites after the oxidation testing by TGA are shown in Fig. 4. For all ZSZ composites, the monoclinic ZrO₂ pattern appears after the oxidation test; the pattern increases in intensity with increases in the ZrC contents of
the as-sintered compacts. The XRD patterns for ZSZ-1 indicate only monoclinic ZrO$_2$. For ZSZ-2, 3, and 4, the intensity of peaks for monoclinic ZrO$_2$ is much smaller than those of the starting particles.

**Figure 5(a)** shows the cross-sectional images of the ZSZ composites after oxidation up to 800°C. Selected EDS analyses for the cross-section of the ZSZ-3 compact are also shown in Fig. 5(b). Similar patterns appear for the other ZSZs in post-oxidation EDS analyses. For oxidation up to 800°C, porous oxidized layers are formed after oxidation. The thickness of the porous oxide layer for ZSZ-1 (~100 µm) is much larger than that for ZSZ-2, 3, and 4 (10–30 µm). The signal from O at the oxidized layer is lower than that of Si and Zr. Therefore, at this temperature region, oxidation proceeds slowly in all samples but ZSZ-1. **Figure 6(a)** also shows cross-sectional images of the ZSZ composites after oxidation up to 1500°C. Selected EDS analyses for the cross-section of ZSZ-3 are shown in Fig. 6(b). ZSZ-2, 3 and 4 oxidized up to 1500°C are coated with porous ZrO$_2$ layers filled with SiO$_2$; some unoxidized surface area remains. From the EDS analysis shown in Fig. 6(b), the signal from Si at the interface between the protective oxide layer and the unoxidized area is weak in comparison with that of Zr at this region. This indicates the formation of a SiC-depleted layer (ZrB$_2$+ZrO$_2$) beneath the layer of ZrO$_2$ and SiO$_2$.

**Figure 7** summarizes the thickness of the oxidized layers in the ZSZ composites. For ZSZ-1, the thickness of the oxide layer reaches 100 µm at 800°C. For ZSZ-2, 3, and 4, the thicknesses of the oxide layers are ~10–30 µm, increasing at ~1000–1200°C to ~40–60 µm. Finally, the thicknesses reach ~60–80 µm. The oxide layer for ZSZ-2 is thicker than that of ZSZ-3 and 4; however, the amount of increase in oxide layer thickness is almost equal in ZSZ-2, 3, and 4.

Generally, ZrB$_2$, SiC, and ZrC react with oxygen according to the following equations:

1. $\text{ZrB}_2(s) + 5/2 \text{O}_2(g) \to \text{ZrO}_2(s) + \text{B}_2\text{O}_3(l)$
2. $\text{SiC}(s) + 3/2 \text{O}_2(g) \to \text{SiO}_2(l) + \text{CO}(g)$
3. $\text{ZrC}(s) + 3/2 \text{O}_2(g) \to \text{ZrO}_2(s) + \text{CO}(g)$

In addition, B$_2$O$_3$ evaporates above 1200°C.

$\text{B}_2\text{O}_3(l) \to 2 \text{B}_2\text{O}_3(g)$

ZrB$_2$ forms a B$_2$O$_3$ layer on the specimen surface at ~800–1000°C and thereafter exhibits oxidation resistance because the B$_2$O$_3$ layer prevents the diffusion of oxygen into the unoxidized area. However, rapid oxidation is observed above ~1100–1200°C owing to the evaporation of the B$_2$O$_3$ layer; this oxidation causes rapid weight gain in this temperature region. SiC also forms a SiO$_2$ layer above ~800°C; this protective layer is maintained at temperatures exceeding 1500°C. ZrC forms porous ZrO$_2$ and gaseous CO (or CO$_2$), with no contribution to oxidation resistance from ~500 to 1500°C.

In the TGA study of the ZSZ-1 specimen [see Fig. 3(a)], a rapid increase in weight is observed from 600 to 800°C and oxidation of ZSZ-1 is nearly complete at 1200°C; only weight loss from the evaporation B$_2$O$_3$ is observed above this temperature. ZSZ-1 has the highest ZrC and the lowest ZrB$_2$ levels among the specimens. Thus, B$_2$O$_3$ layer from the oxidation of ZrB$_2$ does not appear before the rapid oxidation of ZrC occurs. This behavior indicates insufficient B$_2$O$_3$ forms to cover the surface of the compact because the content of ZrB$_2$ is much lower than that of ZrC in ZSZ-1. For the other specimens, the weight increases monotonically from 600 to 1500°C and weight increase rate of them is much smaller than that observed in ZSZ-1 as shown in Fig. 3(b).

For ZSZ-2, 3, and 4, as shown in EDX analysis for ZSZ composites after oxidation up to 1500°C [Fig. 6(b)], SiO$_2$ with ZrO$_2$
layer forms as protective oxide layer on the surface after evaporation of B$_2$O$_3$ above 1100–1200°C; the ZSZ composites thus maintain oxidation resistance up to 1500°C and unoxidized area remains after oxidation up to 1500°C. In addition, the formation of the SiC-depleted layer is detected beneath ZrO$_2$ with SiO$_2$ layer. This result implies that SiC reacts with oxygen to form gaseous SiO at the interface between the protective oxide layer and the unoxidized area. Then, SiO moves toward the surface but oxidizes before reaching the surface. Thus, SiC-depleted regions are formed and SiO$_2$ is supplied to the protective oxide layer. ZrO$_2$ is produced from the beginning of oxidation to the temperature of 1500°C by the oxidation of ZrB$_2$ and ZrC. However, ZrO$_2$ has no oxidation resistance as it is much more permeable to oxygen than SiO$_2$.1),26),27) Furthermore, the ZrO$_2$ formed by the oxidation of ZrB$_2$ and ZrC is porous in structure3),12),28) because the oxidation of ZrB$_2$ and ZrC initiates before the oxidation of SiC at temperatures up to 1200°C; the active oxidation of SiC beneath the protective oxide layer also causes the formation of porous ZrB$_2$ and ZrC layers above 1500°C. These results demonstrate that the progress of oxidation for ZSZ composites strongly depends on the ZrC content: ZSZ composites with less than 50 vol% ZrC and more than 34 vol% of ZrB$_2$ show greater oxidation resistance than ZSZ-1 (64 vol% ZrC, 20 vol% ZrB$_2$). In this study, the ZSZ composite with the lowest content of ZrC (ZSZ-4: 20 vol% ZrC, 64 vol% ZrB$_2$) has the highest oxidation resistance, because ZSZ-4 shows the lowest weight gain and the thinnest oxide layer during TGA testing. On the other hand, as shown in Fig. 7, the result of TGA studies and the thickness of the oxide layer illustrate that the progression of oxidation is independent of the content of ZrC for ZSZ composites containing less than 50 vol% ZrC (ZSZ-2, 3, and 4) after the formation of the protective oxide layer above 800°C.

3.3 In-situ observation of protective oxide layer using HTOS

In-situ observations were performed using the HTOS described in Section 2.3. Figure 8(a) shows image sequences from the ZSZ composites during oxidative exposure at 1500°C. For comparison purposes, scanning electron micrographs (SEM) of the same locations after the test are also shown in the figure. Previous studies22),23) confirmed that the quality of imaging is maintained even at temperatures above 1400°C. In addition, SEM images obtained from the same locations after cooling show the same characteristics as those from the HTOS. This demonstrates that the changes in the captured images above 1400°C are not characteristic of the observation system, but instead depict microstructural changes. Even above the HTOS maximum temperature, the specimen surfaces are clearly visible regardless of composition; the effect of thermal radiation seems quite small. This suggests that the HTOS used in this study can be applied for surface observation in the temperature range of 1400 to 1500°C.

Surface structural changes begin to occur at ~600°C for each specimen, suggesting the oxidation of ZrB$_2$ and ZrC. Radial cracks from the corners of each Vickers impression are clearly visible before the test; however, these cracks are completely covered with oxides at ~800°C, and localized drastic color changes are observed on the surface. With further heating, the initial isolated color-changed circular regions nucleate across the specimen. This behavior is observed in all specimens; however, the nucleation of the island-like regions initiates at 1400, 1500, and 1500°C after 2 min in ZSZ-4, ZSZ-3, and ZSZ-2, respectively.

Figure 8(b) illustrates the relationship between the area density of the islands and the content of ZrC. The area density of islands is defined as the number of islands per observed area. In the present study, the observed area is approximately 2 mm$^2$. The area density of the islands clearly increases with decreases in the
ZrC content. Figures 9(a) and 9(b) depict the relationship between ZrC contents and island sizes, which were measured by image analysis. The average diameter for ZSZ-3 at 1500 and 1500°C after 2 min is \( \bar{120} \) and \( \bar{100} \) µm, respectively. On the other hand, the average diameter for ZSZ-4 at 1400, 1450, 1500, and 1500°C after 2 min is \( \bar{60} \), \( \bar{50} \), \( \bar{50} \), and \( \bar{40} \) µm, respectively. Figures 9(a) and 9(b) reveal that the diameters of the islands decrease with increasing holding times and temperatures. Moreover, the distribution of island diameters decreases with increases in the temperature and holding time and decreases in the content of ZrC in the ZSZ composites. Figure 10 depicts a high-magnification view of the Vickers impressions in each specimen. In some island regions, the centers of the islands are cracked open with increased time. During holding at the maximum temperature, these opened cracks are closed and re-opened. The HTOS is effective in investigating these time-dependent cracking behaviors at high temperatures.

3.4 Oxidation behaviors of ZSZ composites and the effectiveness of HTOS

The effect of the ZrC content on the oxidation behavior was not identified by the weight change and cross-sectional observations, but by the in-situ observation of ZSZ-2, ZSZ-3, and ZSZ-4 above 1400°C. Based on the experimental results, the oxidation

![Fig. 8.](a) Sequences of microstructural evolution of ZSZ composites up to 1500°C. (b) The relationship between area density of islands and the content of ZrC in compacts.)

![Fig. 9.](Relationships among ZrC content and diameters of islands: (a) ZSZ-3 and (b) ZSZ-4.)

![Fig. 10.](High-magnification view around Vickers impressions. Arrow indicates locations of newly formed cracks. Opened cracks close as time proceeds.)
behavior of ZSZ composites can be divided into four stages: Stage I (~500–800°C), Stage II (~800–1200°C), Stage III (1200–1400°C), and Stage IV (~1500°C).

Stage I, II and III: the oxidation of ZSZ composites strongly depends on the content of ZrC. The ZSZ composite containing more than 50 vol% ZrC (ZSZ-1) does not form a protective oxide layer and fully oxidizes up to 1400°C. For ZSZ-2, 3, and 4, a B2O3 layer is formed that suppresses the further oxidation of the composite. Although the B2O3 layer begins evaporating at temperatures above 1200°C, the SiO2 layer forms in this regime and continues to prevent oxidation. These phenomena could be detectable in the post-testing specimens using a conventional electric furnace.13)

Stage IV: From in-situ observation at 1500°C by the HTOS, evaporation of gaseous products occurs in all ZSZ composite specimens. For ZSZ-1, evaporation occurs under the thick porous layer, which is attributed to the CO and SiO2 gases3) formed by the oxidation of SiC and the evaporation of B2O3. Evaporation behavior also occurs in ZSZ-2, 3, and 4; however, the process differs significantly from that in ZSZ-1. Islands nucleate and burst repeatedly, as was reported for the ZrB2–SiC binary system.29) This phenomenon probably originates from the nucleation of gaseous products such as CO, SiO2, and B2O3.5,11)13) Because ZSZ-2, 3, and 4 form protective oxide layers comprising SiO2 and ZrO2, the gaseous products that evolve beneath the protective oxide layer are evacuated to the atmosphere through the layer at 1500°C. The SiO2 does not diffuse toward the surface with the gaseous products because the viscosity of SiO2 is significantly high (~3 x 106 Pa·s at 1500°C).30) Eventually, the gaseous products break the SiO2 layer, or the porous ZrO2 layer with SiO2 regions; this causes the nucleation and bursting of islands on the oxidized surface. Moreover, in comparing the microstructures of the ZSZ composites before oxidation and the diameters of the islands [see Figs. 2(a), 9(a) and 9(b)], the islands on the oxidized surfaces can be attributed to the gas products formed by the oxidation of ZrC. Island formation is mainly caused by CO in the ZSZ composites and the amount of CO evolved by the oxidation of ZrC increases with increases in the content of ZrC in the composite. For ZSZ-1 and 2, small numbers of large-diameter islands are formed below 1400°C, whereas large numbers of small-diameter islands are formed at 1400°C for the others. The number of islands tends to increase with decreases in the volume of ZrC in the specimen. This correlation indicates that the ratio of ZrC particles per unit surface area is decreased by decreasing the volume of ZrC (ZSZ-1: ~60%; ZSZ-4: ~15%). ZrC particles are completely interconnected in ZSZ-1 and 2, whereas ZrB2 particles are fully interconnected in ZSZ-3 and 4 [see Fig. 2(a)]. Therefore, individual islands evolve independently of other islands for ZSZ-3 and 4, which contain less than 50 vol% ZrC. Thus, the average number and diameters of islands during the oxidation process strongly depend on island formation; in-situ observation of ZSZ composites demonstrates this dependence by showing the progress of oxidation over time. The formation temperature of islands decreases with decreases in the content of ZrC in ZSZ composites. The ZSZ composite with the lowest content of ZrC (ZSZ-4) has the lowest formation temperature of islands, below 1500°C. This result suggests that ZSZ-4 has the highest oxidation resistance among the tested ZSZ composites. HTOS reveals the oxidation behavior of the ZSZ composites during oxidation, providing information that cannot be procured from post-testing specimen observation. HTOS is effective for evaluating the oxidation mechanisms of UHTCs. The oxidation mechanism of UHTCs up to 1500°C, as supported by HTOS data, provides fundamental knowledge that is necessary for the clarification of oxidation mechanisms at temperatures higher than 1500°C.

4. Conclusions

In the present study, the oxidation behaviors of ZSZ composites with differing ZrC contents were characterized by conventional thermal and microstructural analyses. Microstructural changes up to 1500°C were also examined using a HTOS to obtain the following results:

1. The oxidation behaviors of ZSZ composites depended significantly on the ZrC content; those with more than 64 vol% ZrC could not form protective oxide layers.
2. Conventional analysis and observation revealed that the ZrC contents affected the amount of ZrO2 formed during oxidation, the thickness of the oxidized layer, and the mass gain and loss behaviors during and after oxidation exposure. In the present study, ZSZ-4 (ZSZ-4: 20 vol% ZrC, 64 vol% ZrB2) had the highest oxidation resistance below ~1500°C.
3. Island-shaped regions nucleated on the surfaces of all specimens at 1500°C. The islands originated from the CO evolved by the oxidation of SiC and ZrC or the evaporation of B2O3. HTOS clearly identified the nucleation locations of islands and allowed the evaluation of the number and diameters of the islands. These microstructural characteristics also strongly depended on the ZrC content.
4. During oxidation tests at 1500°C, the number of islands increased with decreases in the content of ZrC and the diameters of the islands increased with increases in the content of ZrC, as observed by HTOS. Furthermore, HTOS clearly revealed the pathway for oxygen diffusion in the protective oxide layer during oxidation at 1500°C via the closing and re-opening of cracks or islands. Above 1500°C, oxidation proceeded not only by oxygen diffusion through the protective oxide layer but also by oxygen penetration of the unoxidized region through cracks or islands. For the ZSZ composites that showed oxidation resistance up to 1500°C (ZSZ-2, 3, and 4), the evolution of islands probably corresponded to the formation of the protective oxide layer. In order to determine the optimal composition for ZSZ composites, further quantitative analysis of the relationships between the number and diameters of islands during the oxidation progress of ZSZ composites is required.
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