

# Oxidation of ZrC–30 vol% SiC composite in air from low to ultrahigh temperature

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## Abstract

Oxidation of ZrC–30 vol.% SiC is investigated in air using furnace and oxyacetylene torch. The microstructure and phase composition of oxide scales are analyzed via SEM, XRD, and Raman. At 800 and 1100 °C, SiC is embedded in the porous and cracked ZrO<sub>2</sub> scales, which have a single-layer structure and are almost non-protective. At 1300 and 1500 °C, the protective effect of oxide scales is enhanced by the formed SiO<sub>2</sub>. The scales consist of two subscales, outer and inner layers, during oxidation at 1300 °C for ≥1 h, and 1500 °C for ≥15 min. The growth kinetics of both layers is analyzed. At ~1700 °C, a new layer is observed between the outer and inner layers, which should contain less carbon than the inner layer. At ~2100 °C, the oxide scale is porous and contains many big holes. This scale shows a single-layer structure, which mainly consists of ZrO<sub>2</sub>.

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## 1. Introduction

Interest in ultrahigh-temperature ceramics (UHTCs) has increased significantly in recent years due to the drive to produce a thermal protection system and other components for hypersonic aerospace vehicles.<sup>1–3</sup> Zirconium carbide (ZrC) is an important member of UHTCs. Besides its high melting temperature, ZrC has a unique combination of high fracture strength, high electrical and thermal conductivity, and resistance to erosion/corrosion.<sup>4–6</sup>

Oxidation resistance is a major issue in the development of UHTCs, but ZrC has a poor high-temperature chemical stability in oxidizing atmosphere, which significantly limits its actual application as UHTCs. Previous reports indicated that ZrO<sub>2</sub> scales on ZrC can be divided into two layers.<sup>7–12</sup> The outer layer is porous and cracked, containing a small amount of free carbon. Pores and cracks in the outer layer offer channels for inward diffusion of oxygen. So, the outer layer is non-protective. The inner layer is relatively dense and rich in carbon, which attracts

lots of attention in the past several years. This layer is considered as a barrier for the diffusion of oxygen during oxidation. However, the inner layer is very thin; that is to say, oxide scale on ZrC mainly consists of the porous and cracked outer layer. Cracks in the outer layer penetrate easily into the inner layer, accelerating the oxidation of matrix. So, the oxide scale on ZrC is almost non-protective, which is confirmed by the linear or approximately linear oxidation kinetics.<sup>7,9,13,14</sup>

A common approach to improve oxidation resistance of UHTCs is the incorporation of Si-containing compounds into UHTCs matrix to form a protective SiO<sub>2</sub>-containing oxide scale.<sup>15–18</sup> However, the reports are scarce by far on oxidation of ZrC-based composites with additives of Si-containing compounds, and some results deviate from that expected. Pierrat et al.<sup>19</sup> investigated the oxidation resistance of pressureless-sintered ZrC–20 vol.% MoSi<sub>2</sub> using an experimental facility called REHPTS. The results showed that addition of 20 vol.% MoSi<sub>2</sub> was detrimental to the oxidation behavior of ZrC in the temperature range of 1800–2400 K, because of its dissociation and its role in the surface melting. Li et al.<sup>20</sup> prepared a ZrC–SiC coating on 2D C/ZrC–SiC composites by chemical vapor deposition and investigated the oxidation behavior of this composites at 1800 °C using CH<sub>4</sub> combustion wind tunnel. The results

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indicated that no protective oxide scale was formed, because ZrC was oxidized completely very fast, and SiC or its oxide SiO<sub>2</sub> was easily blown off. Zhao et al.<sup>21</sup> prepared C/ZrC–SiC by polymer infiltration and pyrolysis process. Furnace test at 1200 °C in air indicated that introduction of 1.9 vol.% SiC can improve the oxidation resistance of C/ZrC, due to formation of dense SiO<sub>2</sub> glass.

In this study, we investigated the oxidation behavior of hot-pressed ZrC–30 vol.% SiC in air from low to ultrahigh temperature using furnace and oxyacetylene torch. The structure evolution of oxide scales was described and discussed. Some interesting phenomena were reported which have not been found in previous works.

## 2. Material and methods

ZrC–30 vol.% SiC composite was referred as ZrC–30SiC below. The starting powders were ZrC (mean particle size 2.1 μm, >98% purity, Changsha Wing High High-Tech New Materials Co., Ltd., China), SiC (β-SiC, mean particle size 2 μm, >99% purity, Central Iron & Steel Research Institute, China). The powder mixture of ZrC–30 vol.% SiC was ball milled in ethanol for 24 h and then dried. Mixed powders were then uniaxially hot pressed in boron nitride-coated graphite die at 2000 °C for 60 min under an argon atmosphere with an applied pressure of 30 MPa. Bulk density and theoretical density were evaluated using the Archimedes method and the rule of mixtures, respectively. Sample coupons in the size of 4.9 mm × 5.8 mm × 6.6 mm were cut from the hot-pressed specimens, and all surfaces were diamond polished to a 1 μm finish. Coupons were ultrasonically cleaned in acetone and alcohol, and then exposed to air at temperature of 800, 1100, 1300 and 1500 °C, respectively, for 15 min to 4 h. The oxidation experiment was conducted in a box furnace with MoSi<sub>2</sub> heating elements. The weight of samples before and after oxidation was carefully measured using a precision balance with an accuracy of 10<sup>−5</sup> g. Sample coupons with dimension of Φ17.4 × 12.7 mm were used in the oxidation experiment at temperature of ~1700 and ~2100 °C, which was carried out with the oxyacetylene torch facility of Hu et al.'s group.<sup>22,23</sup> The oxyacetylene torch test was conducted under two different conditions. During the first test, after several adjustments of gas flow rate, the pressure and flux of acetylene were fixed at 0.1 MPa and 0.32 m<sup>3</sup> h<sup>−1</sup>, and for oxygen 0.5 MPa and 0.64 m<sup>3</sup> h<sup>−1</sup>, respectively. The test time was about 13 min. The sample surface achieves a temperature of 1670 °C within about 3 min, and then it gradually increases to 1700 °C. During the second test, the pressure and flux of acetylene were 0.1 MPa and 0.75 m<sup>3</sup> h<sup>−1</sup>, and for oxygen 0.5 MPa and 1.5 m<sup>3</sup> h<sup>−1</sup>, respectively. The test time was about 10 min. The temperature of sample surface increases sharply to 2060 °C and then gradually reaches to the maximal value of 2200 °C. The phase composition of oxide scale was identified using X-ray diffractometer and Raman spectroscopy. X-ray diffraction (XRD) was carried out in a D/max-2200VPC diffractometer (Rigaku, Tokyo, Japan) with Cu Kα radiation. The Raman spectra were recorded using the 458 nm line from an argon ion laser using a Raman system (JY HR800, Paris, France). The surface

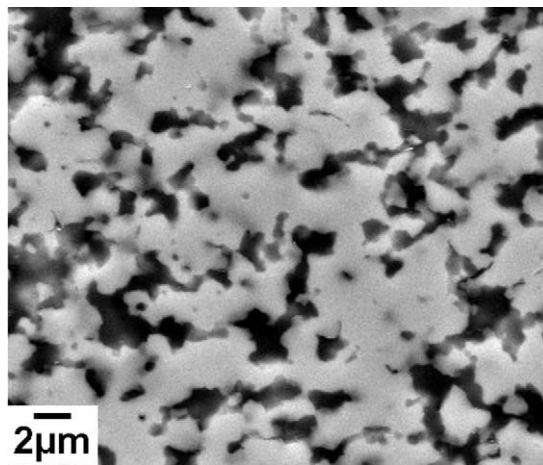


Fig. 1. SEM micrograph of the polished surface of ZrC–30SiC.

and cross section of oxidized samples were observed by scanning electron microscope (SEM, FEI Quanta 200F, Eindhoven, the Netherlands). An optical microscope (Axiovert 40MAT, Germany) was also employed to observe the cross section of oxide scale and determine its thickness.

## 3. Results

### 3.1. Density and microstructure

The measured bulk density of ZrC–30SiC is 5.56 g/cm<sup>3</sup>, which corresponds to a relative density of 98.4%. Fig. 1 shows a SEM micrograph of the polished surface of ZrC–30SiC. The dark and grey phases are SiC, and they appear to be uniformly dispersed in the light ZrC matrix. The different contrast of SiC should be related to their different crystallographic orientations.<sup>24,25</sup> Microstructure of the composite is regular, and few pores are observed on the polished surface, which supports the result of density measurement.

### 3.2. Oxidation at low temperature range (800 and 1100 °C)

XRD analysis (Fig. 2a) indicates that the oxide scale formed at 1100 °C for 15 min consists of *m*-ZrO<sub>2</sub>. Fig. 3a shows the surface SEM micrograph of this scale. It is cracked and porous. SiC is embedded in ZrO<sub>2</sub>. Because the strongest peak of SiC (1 1 1) at 35.6° and the peaks of *m*-ZrO<sub>2</sub> (2 0 0) at 35.3°, ( $\bar{1}$  0 2) at 35.9° are too close to be distinguished, SiC is difficult to detect by XRD in *m*-ZrO<sub>2</sub> matrix. Cross-section SEM micrograph (Fig. 3b) indicates that the oxide scale has a single-layer structure. Its thickness is about 290 μm, and mass gain of sample is 177.9 g/m<sup>2</sup>. Fig. 4 shows the Raman spectrum of this scale. Two broad peaks appear around 1350 cm<sup>−1</sup> and 1600 cm<sup>−1</sup>, corresponding to the A<sub>1g</sub> mode associated with amorphous carbon and E<sub>2g</sub> with graphite, respectively.<sup>8</sup> Fig. 5 shows the specific mass-change as a function of exposure time for ZrC–30SiC during oxidation at 800 and 1100 °C. The kinetics follows an approximately linear law, indicating that the oxidation proceeds mainly via interface limited reaction.

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