

OXIDATION MECHANISMS OF ZrB₂-BASED ULTRA HIGH TEMPERATURE CERAMIC MATRIX COMPOSITES

Ryo Inoue, Tokyo University of Science
inoue.ryo@rs.tus.ac.jp

Yasuo Kogo, Tokyo University of Science

Yuki Kubota, Structures and Advanced Composite Research Unit, Japan Aerospace Exploration Agency (JAXA)
Ken Goto, Institute of Space and Astronautical Science, Japan Aerospace Exploration Agency (JAXA)

Key Words: Ultra High Temperature Ceramics (UHTCs), ZrB₂, Composites, Oxidation, Mechanical properties

Ultra-high temperature ceramics (UHTCs) are expected as the materials for the nose cones and leading edges for hypersonic and re-entry vehicles. Zirconium diboride (ZrB₂) and its composites are a widely studied class of UHTCs. The oxidation of monolithic ZrB₂ forms ZrO₂ and B₂O₃. B₂O₃ acts as a surface protective layer; however, it evaporates above 1200°C. SiC particles are considered effective additives because the SiO₂ formed by the oxidation of SiC protects the unreacted region. Simultaneously, excessive pores are formed under the surface in the SiC particle-dispersed ZrB₂ matrix (hereafter denoted ZS) composites in a wide temperature range by the preferential oxidation of SiC (active oxidation of SiC) because solid SiO₂ is not formed; instead, gaseous SiO forms by active oxidation because of the low oxygen partial pressure relative to that of the surface. The pore-rich porous layer is denoted the "SiC-depleted layer". The SiC-depleted layer leads to spallation and delamination of the oxidized regions on the surface because strength and stiffness of this layer are quite low. Thus, excessive pore formation in ZS composites should be prevented to improve the oxidation resistance. The objective of this study is to understand oxidation mechanisms of ZrB₂-based composites and to propose the way to prevent the formation of SiC-depleted layer in ZS composites. In the present study, we fabricated monolithic ZrB₂, ZS, and ZrB₂-SiC-ZrC (ZSZ) ternary composites by spark plasma sintering (SPS) technique. In addition, carbon fiber-reinforced ZSZ matrix (C/ZSZ) composites was also fabricated by Si melt infiltration (MI) process. Oxidation resistance of monolithic ZrB₂, ZS, ZSZ, and C/ZSZ have specially designed fast heating system in order to characterize oxidation resistance above 2000°C.

The experimental results of the oxidation test for ZS composite with different SiC content showed that the morphologies of the oxidized ZS composites depended strongly on the SiC content. The formation mechanism of SiC-depleted layers beneath the surface scale above 2000°C differed completely from that below 2000°C. Above 2000°C, SiC-depleted layers were formed because the oxygen partial pressure of the air atmosphere was not enough to form SiO₂ by the oxidation of SiC. It was determined that ZrB₂-20vol% SiC showed the best oxidation resistance above 2000°C at high heating rates.

The formation of the oxide layer in ZSZ composites with different ZrB₂/ZrC ratio oxidized above 2000°C was also shown to depend on the ZrC content. The morphologies of ZSZ composite with high and low ZrC content are shown in Fig.1. Volume expansion during the conversion of ZrC to ZrO₂ contributed to the formation of an oxide layer on the surface. The ZSZ composite with the highest ZrC amount had the best oxidation resistance, while volatility diagrams showed the preferential oxidation of ZrC over ZrB₂ and SiC above this temperature. This study clearly showed the efficacy of ZrC as an additive for enhancing the oxidation resistance of ZS composites.

Oxidation behavior of C/ZSZ composites fabricated by MI process was also examined. The effect of fiber addition on oxidation behavior will be discussed based on thermodynamic analysis and experimental results.

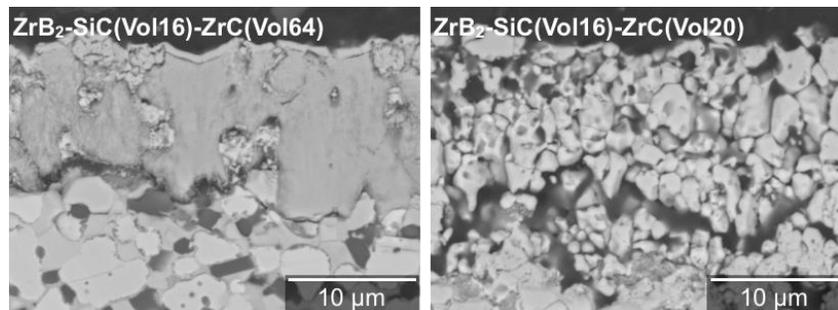


Figure 1 Typical SEM photographs of ZSZ composites after oxidation testing. left: high ZrC content (64vol%), right: low ZrC content.