Oxidation Mechanisms of Reaction-Bonded Silicon Nitride
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Abstract
The oxidation behavior of porous reaction-bonded silicon nitride has been investigated in the temperature range 900-1400°C for up to 3 hours by the Simultaneous Thermal Analysis technique. The mechanism of oxidation is complex and depends critically on the temperature. At low temperatures in excess oxygen, a protective silica film is formed by passive oxidation. The low Po2 in pores beneath the film leads to active oxidation of both the silicon nitride and silicon oxynitride which may be formed during fabrication process. A model for the roles of the silica film and the silicon oxynitride was proposed and discussed.

1. Introduction
Silicon nitride based ceramics among the most promising materials for high-temperature structural applications because of their excellent thermomechanical properties. Among various silicon nitride ceramics, reaction-bonded silicon nitride (RBSN) exhibits low thermal expansion giving rise to good thermal shock resistance, low mass density, relatively high strength, good resistance to oxidation and good refractoriness.1

Many researchers 2-3 has shown that the open porosity which is characteristic of RBSN can degrade both high- and low- properties through complex oxidation-related mechanisms that are not observed in fully-densed materials. These complexities arise because oxygen can interact with silicon nitride all surface throughout porous body leads to the formation of SiO2 scale on the surface and interlayer of Si3N4O during the oxidation process.4

The purpose of this study is to systematically examine the initiation of oxidation kinetics through several parameters. A model for the oxidation phenomena is proposed and discussed in order to facilitate the understanding of the oxidation mechanisms.

2. Experimental Procedure
The silicon compacts were made by mixing a commercial grade silicon (98% purity) with polyvinyl alcohol 3 mol%, uniaxial pressing the mixture at 72 MPa into a rectangular bar, followed by cold isostatic pressing (CIP) at 300 MPa. The specimens were pre-sintered in argon at 1200°C and then nitrided in a nitrogen atmosphere with a heating rate of 10°C/ min up to 1500 °C for 3 hrs in a graphite crucible. The oxidation test was conducted in a Simultaneous Thermal Analysis instrument with a heating rate of 5°C/min up to 1400°C in air. Isothermal experiments were conducted separately at 900-1400°C for 3 hrs. The microstructure of the sample after oxidation was examined using a scanning electron microscope.

3. Results and Discussion
Negligible weight change was observed at isothermal experiments lower than 900°C. At 1100°C, significant weight gain increased and a rapid mass increase of oxidation began at 1200°C. Finally, the specimen gradually lost weight at 1400°C.

Fig.1. Isothermal thermogravimetric obtained from oxidation in air at 900°C to 1400°C.

Fig.2 SEM micrographs of RBSN sample surfaces exposed to air (a) 900 °C (b) 1200 °C (c) 1300°C (d) 1400°C, respectively

Fig. 3 Schematic drawing of oxidation mechanisms RBSN

4. Conclusion
The oxidation mechanisms of porous reaction-bonded silicon nitride exposed to air takes into account two concurrent processes occurring within the pore channels; i.e. the diffusive flow of oxygen and the consumption of oxygen by reaction with Si3N4 at the channel walls to form silica. As temperature increased, the reaction rate initially occurred with exponential increment and then dwindled with less accessible surface until a protective silica film was formed (passive oxidation). With diminishing Po2 in the pores beneath the film, SiO gas was generated by active oxidation. The reactions were further complicated by the formation of the Si3N4O which is formed in excess oxygen or with liquid silica.

References