



## Short Communication

# Dramatic influence of interface chemical potentials on the oxidation of silicon and carbon based compounds

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## Abstract

At ultrahigh temperatures silicon and carbon based ceramics can either decompose vociferously by reacting with oxygen, or grow a passivation scale of silica, that prevents it. We show that this transition in silicon oxycarbonitride ceramics when heated to 1500 °C in variable oxygen pressure is tied to the interfacial chemical potential, or the virtual partial pressure of carbon-monoxide at the interface, which can be sustained only when the silica layer is growing.

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## 1. Introduction

Silicon and carbon based ceramics, the next generation high-temperature structural materials, hold the potential to produce quantum leaps in the operating temperatures of gas turbines.<sup>1</sup> The oxidation behavior of these materials is one of the key scientific and technological issues. Traditional studies of oxidation of SiC and polymer-derived silicon oxycarbonitride ceramics have focused on oxidation behavior in terms of the atmospheric conditions.<sup>2</sup> However, the thermodynamic balance between active decomposition and protection offered by the silica overgrowth depends on the activity, or the virtual partial pressure, of the products of the interfacial reaction. For example, carbon reacts to produce carbon-monoxide (CO). In the absence of the silica scale this reaction leads to rapid weight loss. But in the presence of a silica scale the interface activity of CO can rise very significantly if its diffusion through the silica overgrowth is slow. This high interfacial activity creates a back potential that can prevent active decomposition of silicon carbide.

Silicon and carbon based ceramics are broadly separated into two classes: binary, stoichiometric silicon carbide (SiC) and more complex chemistries, also known as polymer derived ceramics (PDCs), that are composed of SiCNO in various

mole fractions. The essential difference between them is that while SiC requires oxygen from the atmosphere to decompose  $\{\text{SiC(s)} + \text{O}_2(\text{g}) \rightarrow \text{SiO(g)} + \text{CO(g)}\}$ , the PDCs can lose weight spontaneously consuming the oxygen within them. As a result the active to passive oxidation transition in SiC is complex since the passivation and active decomposition reactions compete for the oxygen molecules arriving at the surface from the atmosphere. In an inert atmosphere SiC is immune to oxidation.

In contrast the PDCs will decompose in an inert atmosphere since the decomposition reaction occurs with the oxygen residing within the compound. The present communication considers the simpler case of a SiCNO compound to study the transition between weight-loss, which occurs in an inert environment, and weight-gain which requires an oxidizing atmosphere.

It is to be noted that the active to passive oxidation transition in SiC can share the same fundamental explanation as the weight-loss to weight-gain transition in SiCNO.

## 2. Experimental results

The SiCNO powder was prepared from a liquid precursor, Ceraset<sup>®</sup> obtained from KiON Defense Technologies Inc., Hunting Valley, PA. The liquid was cross-linked into a rigid polymer at 300 °C under flowing argon for 4 h in a quartz tube furnace. The cross-linked resin was crushed into powder using a mortar and pestle and milled in a dry high-energy ball mill, and

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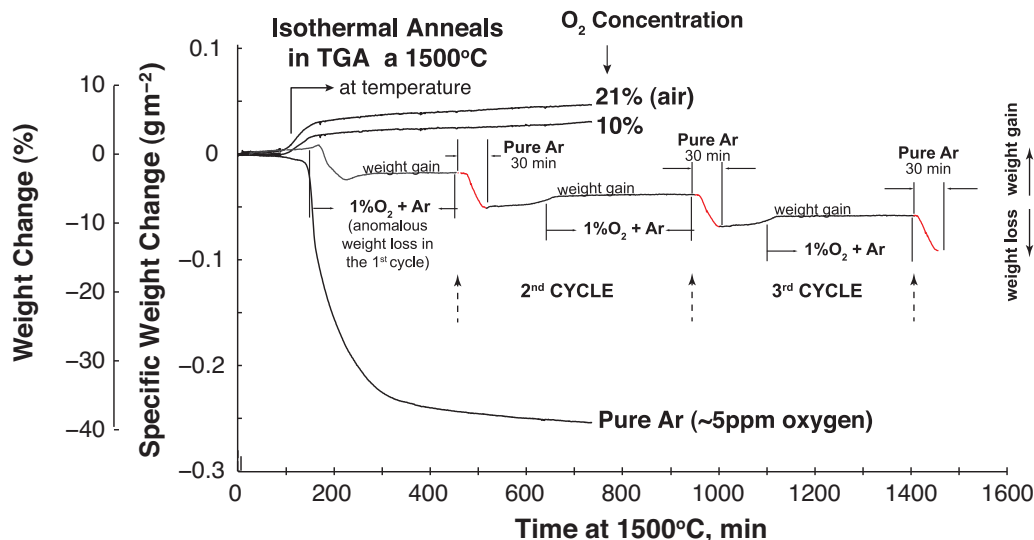


Fig. 1. Weight loss and weight gain in SiCNO when exposed to different oxygen atmospheres at 1500 °C.

then pyrolyzed at 1000 °C in an alumina tube furnace for 2 h in argon. The chemical composition of the pyrolyzed powders was  $\text{Si}_{0.35}\text{C}_{0.29}\text{N}_{0.32}\text{O}_{0.03}$ , measured by the procedure described in Ref.<sup>3</sup> The powders had particles in the 1–20  $\mu\text{m}$  range. Specific surface area of the powder was measured to be  $1.55 \text{ m}^2 \text{ g}^{-1}$  by a nitrogen adsorption BET (Model ASAP 2010, Micromeritics Instrument Corp., Norcross, GA).

The weight change experiments were carried out in a Netzsch TGA apparatus (Model STA409, Netzsch-Geratebau GmbH, Selb, Germany) in four different atmospheres: ambient air ( $p_{\text{O}_2} = 0.21$ ), 10% $\text{O}_2$  ( $p_{\text{O}_2} = 0.1$ ) in Ar, 1% $\text{O}_2$  ( $p_{\text{O}_2} = 0.01$ ) in Ar, and ultrapure Ar containing  $\sim 5$  ppm oxygen ( $p_{\text{O}_2} = 5 \times 10^{-6}$ ). Oxygen concentration was measured by a trace oxygen analyzer (Model 2001RS, Advanced Micro Instruments, Inc., Huntington Beach, CA). The samples were placed in silicon carbide crucibles. The furnace was ramped up to 1500 °C in approximately 145 min ( $10 \text{ }^\circ\text{C min}^{-1}$ ) and then held at that temperature.

The measurements of the weight change as a function of the atmospheric oxygen pressure at 1500 °C are shown in Fig. 1. They extend up to 600 min for experiments carried out in ambient air, in 10% $\text{O}_2$  + Ar and in ultrapure Ar: the first two cases are marked by weight gain while there is weight loss of more than 40% in ultrapure Ar.

In the case of (1% $\text{O}_2$  + Ar) the atmosphere was switched between pure Ar and (1% $\text{O}_2$  + Ar) in three cycles. In each cycle approximately 300 min were spent in 1% $\text{O}_2$  followed by 30 min in pure Ar. Weight gain in  $\text{O}_2$  is repeatedly followed by weight loss in Ar. The gradual weight gain after the 1% $\text{O}_2$  is switched on stands in contrast to the nearly immediate onset of rapid weight loss upon the change to pure Ar. The weight gain is tied to the gradual build up of back pressure of CO at the interface as the silica passivation layer begins to grow again. In contrast the immediate onset of weight loss is consistent with the concept that weight-loss begins as soon as the oxide stops growing and the interfacial pressure of CO falls below a threshold value.

In the first cycle the 1% $\text{O}_2$  case shows some weight loss before beginning to show weight gain in oxidizing atmosphere. Subsequent cycles do not show this anomalous behavior, which is ascribed to a different chemistry on the surface of the PDC particles that is more prone to weight loss. Once this layer is consumed by weight loss then self-consistent cycling behavior is achieved. A different chemistry on the particle surface to a thickness of  $\sim 150$  nm has been reported in the literature<sup>4</sup> and has been attributed to the peculiarities of the conversion of the polymer into the ceramic; it may be a result of trace amounts of oxygen present in the Ar atmosphere during pyrolysis of the polymer.

### 3. Analysis

#### 3.1. The concept

Carbothermal decomposition produces gaseous species of specific partial pressure determined by thermodynamic equilibrium. It is immediately evident that if an atmosphere of the same gaseous species, but of a higher partial pressure is imposed extrinsically on the ceramic, then carbothermal decomposition would stop. For example decomposition of silicon-nitride into nitrogen and silicon can be halted by an overpressure of nitrogen. Since the equilibrium nitrogen pressure increases with temperature, this result can be expressed in a “map” by creating a locus of the equilibrium nitrogen pressure as a function of temperature. If the overpressure lies above this locus then silicon nitride will be prevented from decomposing.<sup>5</sup>

The analysis presented here is based upon the same concept. However, decomposition is prevented not by creating an extrinsic overpressure of the gaseous products, but by the interfacial partial pressure of these same species that is introduced by the kinetic constraints in the growth of the oxide scale. The kinetic constraint means that the interfacial activity of a species is determined by how fast it can diffuse through the silica overgrowth.

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