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HIGH TEMPERATURE ALKALI CORROSION OF CERAMICS IN COAL GAS

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Objective/Scope

High temperature alkali corrosion has been known to cause premature failure of ceramic components used in advanced high temperature coal combustion systems such as coal gasification and clean-up, coal fired gas turbines, and high efficiency heat engines. The objective of this research is to systematically evaluate the alkali corrosion resistance of the most commonly used structural ceramics including silicon carbide, silicon nitride, cordierite, mullite, alumina, aluminum titanate, zirconia, and fireclay glass. The study consists of identification of the alkali reaction products (phase equilibria) and the kinetics of the alkali reactions as a function of temperature and time.

Technical Progress

I. Phase Equilibria

The soda-zirconia phase relations were investigated in the region from 0-40 wt% soda and from 840-1500°C. Samples were prepared by repeatedly grinding and mixing appropriate amounts of sodium carbonate and zirconia in acetone with a glass mortar and pestle, drying, and packing into platinum tubes. The samples fired at temperatures higher than 900°C were first calcined at 840°C to remove carbon dioxide from the carbonate, and sealed in platinum tubes, followed by isothermal soaking at temperatures ranging from 900 to 1500°C. The phases formed after the heat treatments and the phase transition temperatures of the soda-zirconia reactions were determined using x-ray diffraction (XRD) and differential thermal analysis (DTA), respectively.

Table 1 lists the compositions and the phase assemblages of the soda-zirconia reactions at different temperatures. The reaction products consist of sodium zirconate (Na_2ZrO_3), and zirconia for all the compositions studied. DTA analysis of the samples showed the tetragonal to monoclinic zirconia transformation at 1170°C; however, only the monoclinic phase was detected in the quenched samples due to the martensitic transformation below 1170°C. No melting was observed in the DTA analysis up to 1400°C for the soda-zirconia system.

II. Alkali Corrosion Kinetics

The bubbler used to generate alkali vapors was modified for the corrosion study. The previous setup consisted of a steel vessel connected to the tube furnace by stainless steel pipes. The vessel and pipes were heated to 800°C to generate a sufficient concentration of alkali vapors for the corrosion studies. The flow of the compressed air (used as the carrier gas for the alkali vapors) was completely stopped in some cases after a day or two of operation. The stainless steel pipe had oxidized and/or reacted with the alkali vapors, completely blocking the flow through the pipe. To alleviate this problem a platinum cap on an alumina crucible and platinum tubing were used. The compressed air, which was used as a carrier gas, was flowed through sodium hydroxide deposited on silica (Ascarite) to remove the carbon dioxide and activated alumina to remove the water before entering the reaction chamber. The concentration of the alkali vapors, measured by the weight loss of sodium nitrate from the bubbler, was approximately 24 vol%.

Due to reaction with alkali vapors, a glassy layer was formed on the surface of the SiC specimen following the 1000°C exposure test. After dissolving the glassy layer in acid, the reaction thickness of SiC at 1000°C was measured as a function of exposure time, as shown in Figure 1(a). The relationship is not linear as would be expected if the process is reaction controlled. The thickness squared versus time is shown in Figure 1(b). The linear relationship between the thickness squared and time suggests that the reaction is controlled by the oxygen diffusion through the glassy layer.

The corrosion experiments of SiC will be extended to other temperatures between 800 and 1100°C for the next report period. The soda-calcia stabilized cubic zirconia phase relations will be investigated also.

Table 1. Phase Analysis of the Soda-Zirconia System

Composition (wt%)			
Zirconia	Soda	Temperature (°C)	Phases
95	5	840	m-ZrO_2 + Na_2ZrO_3 (tr)
		900	m-ZrO_2 + Na_2ZrO_3 (tr)
		1000	m-ZrO_2 + Na_2ZrO_3 (tr)
		1100	m-ZrO_2 + Na_2ZrO_3 (tr)
		1200	t-ZrO_2 + Na_2ZrO_3 (tr)
		1300	t-ZrO_2 + Na_2ZrO_3 (tr)
		1500	t-ZrO_2 + Na_2ZrO_3 (tr)
90	10	840	m-ZrO_2 + Na_2ZrO_3
		900	m-ZrO_2 + Na_2ZrO_3
		1000	m-ZrO_2 + Na_2ZrO_3
		1100	m-ZrO_2 + Na_2ZrO_3
		1200	t-ZrO_2 + Na_2ZrO_3
		1300	t-ZrO_2 + Na_2ZrO_3
		1500	t-ZrO_2 + Na_2ZrO_3
85	15	840	m-ZrO_2 + Na_2ZrO_3
		900	m-ZrO_2 + Na_2ZrO_3
		1000	m-ZrO_2 + Na_2ZrO_3
		1100	m-ZrO_2 + Na_2ZrO_3
		1200	t-ZrO_2 + Na_2ZrO_3
		1300	t-ZrO_2 + Na_2ZrO_3
		1500	t-ZrO_2 + Na_2ZrO_3
80	20	840	m-ZrO_2 + Na_2ZrO_3
		900	m-ZrO_2 + Na_2ZrO_3
		1000	m-ZrO_2 + Na_2ZrO_3
		1100	m-ZrO_2 + Na_2ZrO_3
		1200	t-ZrO_2 + Na_2ZrO_3
		1300	t-ZrO_2 + Na_2ZrO_3
		1500	t-ZrO_2 + Na_2ZrO_3
70	30	840	m-ZrO_2 (tr) + Na_2ZrO_3
		900	m-ZrO_2 (tr) + Na_2ZrO_3
		1000	m-ZrO_2 (tr) + Na_2ZrO_3
		1100	m-ZrO_2 (tr) + Na_2ZrO_3
		1200	t-ZrO_2 (tr) + Na_2ZrO_3
		1300	t-ZrO_2 (tr) + Na_2ZrO_3
		1500	t-ZrO_2 (tr) + Na_2ZrO_3

tr = trace

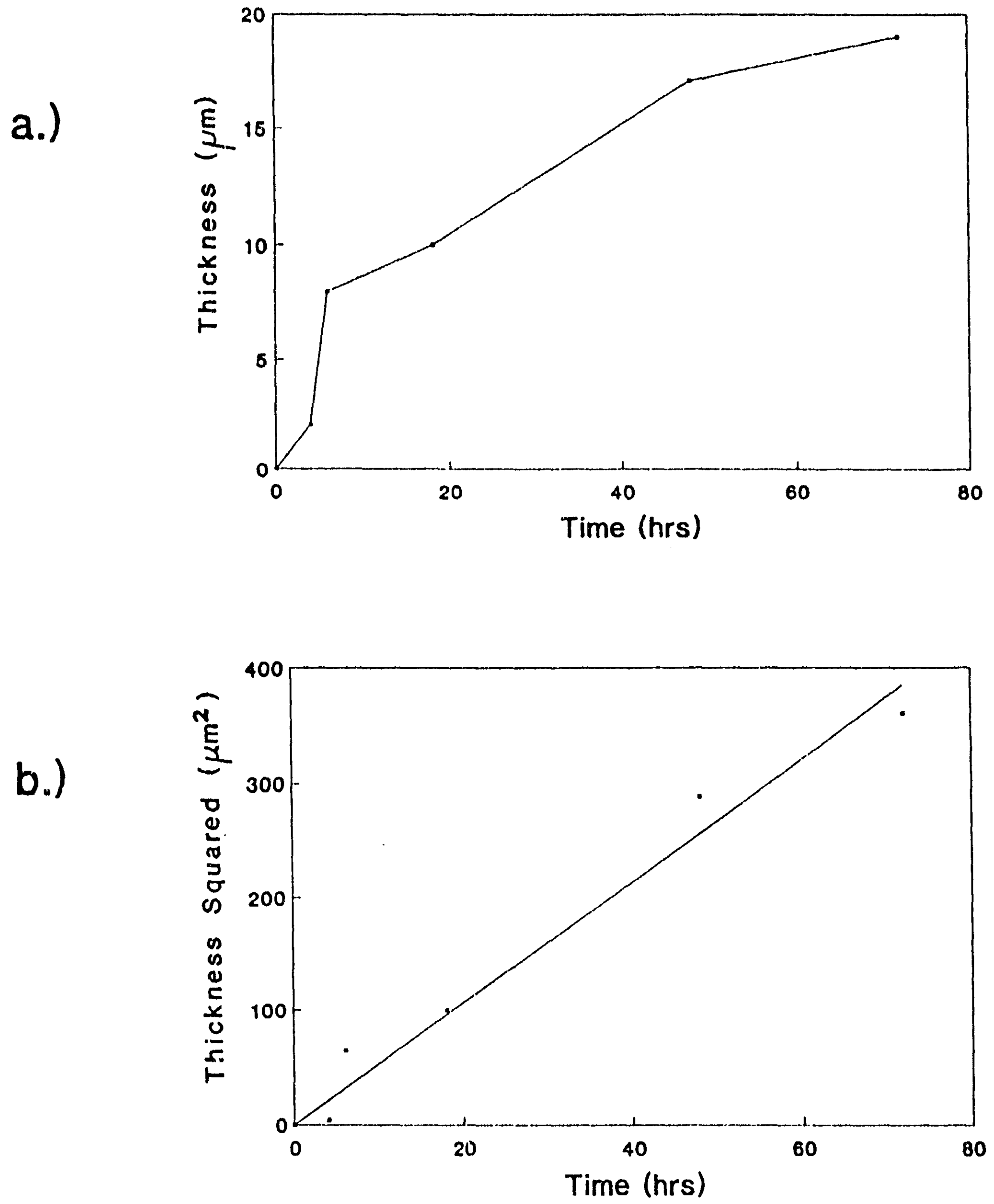

Figure 1. a.) Reaction thickness versus time for SiC at 1000 C and 24 vol.% alkali concentration
b.) Reaction thickness squared versus time

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