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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 potassia-cordierite phase relations were investigated in the region from 0-32 wt% potassia and from 840-1100°C. Samples were prepared by repeatedly grinding and mixing appropriate amounts of potassium carbonate and pure cordierite in acetone with a glass mortar and pestle, drying, and packing into platinum tubes. The cordierite powders were derived from sol-gel synthesis using magnesium nitrate, aluminum tri-sec butoxide, and tetraethyl orthosilicate as precursors. The samples fired at temperatures higher than 840°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 1100°C for 114 to 144 h. The low temperature heat treatment at 840 °C was conducted in air because the weight loss of potassium carbonate measured at the same temperature was negligible. The phases formed after the heat treatments and the solidus temperatures of the potassia-cordierite system were determined using x-ray diffraction (XRD) and differential thermal analysis (DTA), respectively.

Table 1 lists the compositions investigated and the potassia-cordierite reaction products at different temperatures. For compositions containing less than 24 wt% potassia, XRD and DTA analyses indicate that cordierite was decomposed by potassia to form kaliophilite and forsterite below the solidus temperatures. As determined by XRD, the amounts of kaliophilite and forsterite increased with potassia content at all temperatures, and cordierite was completely decomposed at 24 wt% potassia. For compositions containing 32 wt% potassia, the equilibrium phases consisted of kaliophilite, K_2MgSiO_4 , and an unknown phase.

As shown in Table 2, the solidus temperature appeared to vary with potassia content, ranging from 1200°C at 9% potassia to 1408°C at 24% potassia. For the 32% potassia sample the solidus was at 1380°C and for the 3% sample the solidus was 1430°C as determined by the DTA scans.

II. Alkali Corrosion Kinetics

The experimental setup from which alkali vapors were generated and transported

to the specimen chamber was modified in an attempt to increase the reproducibility of the corrosion results on SiC samples. The SiC samples used were approximately 5x5x10 mm. The pellets were wrapped in platinum foils and mounted in a platinum sample holder. Four samples were used for each run to determine the reproducibility within a run. The samples were exposed to alkali vapors at 1000°C for 45 h, followed by air-quenching. The alkali vapors were generated by melting sodium nitrate at 800°C. A glassy layer containing gas bubbles was formed on the surface of the SiC following the exposure. EDX analysis of the exposed samples showed that in addition to sodium, iron was also present on the surface of the SiC. Examination of the bubbler after the exposure test revealed that the salt had significantly corroded the inside of the bubbler. A mullite tube (closed end) was used as a liner in order to decrease the attack on the bubbler, and the system was reconstructed to avoid the dissolution of iron (tubing) in the molten salt. X-ray diffraction analysis of the salt which remained in the bubbler after running for one week revealed that both sodium carbonate and sodium nitrate were present. The sodium carbonate was probably formed from the reaction of sodium nitrate with carbon dioxide in the compressed air. The formation of sodium carbonate drastically reduced the concentration of alkali vapors because of the high melting temperature of sodium carbonate (851°C). A carbon dioxide absorbent and a moisture absorbent will be installed to prevent the conversion of sodium nitrate to sodium carbonate and the introduction of steam to the system.

Three exposure tests conducted at 1000°C for 24 h in the modified system yielded an average change of 0.020 mm in sample thickness with a standard deviation

of 0.004 mm after removal of the glassy layer in boiling water.

The corrosion measurements of silicon carbide will be extended to longer corrosion times and different temperatures. The phase relations in the zirconia-soda and aluminum titanate-soda systems will be investigated also for the next report period.

Table 1. Phase Analysis of the Potassia-Cordierite System

Composition (wt%)		Temp. (°C)	Phases
Cordierite	Potassia		
91	9	840	cordierite, kaliophilite, forsterite (tr)
		900	cordierite, kaliophilite, forsterite (tr)
		1000	cordierite, kaliophilite, forsterite (tr)
		1100	cordierite, forsterite, unknown
84	16	840	cordierite, kaliophilite, forsterite
		900	cordierite, kaliophilite, forsterite
		1000	cordierite, kaliophilite, forsterite
		1100	cordierite, kaliophilite, forsterite
76	24	840	kaliophilite, forsterite
		900	kaliophilite, forsterite
		1000	kaliophilite, forsterite
		1100	kaliophilite, forsterite
68	32	840	kaliophilite, KMS
		900	kaliophilite, KMS
		1000	kaliophilite, KMS
		1100	kaliophilite, KMS, unknown

tr = trace; KMS = K_2MgSiO_4

Table 2. Solidus Temperature of the Potassia-Cordierite System

Potassia Content (wt%)	Solidus Temperature (°C)
3	1430
9	1200
16	1280
24	1408
32	1380

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