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HIGH TEMPERATURE ALKALI CORROSION OF CERAMICS

IN COAL GAS

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Summary

The high temperature alkali corrosion kinetics of SiC have been systematically investigated from 950 to 1100°C at 0.63 vol% alkali vapor concentration. The corrosion rate in the presence of alkali is approximately 10^4 to 10^5 times faster than the oxidation rate of SiC in air. The activation energy associated with the alkali corrosion is 406 kJ/mol, indicating that the corrosion process is highly sensitive to temperature changes. The overall reaction appears to be controlled by the oxidation of SiC.

The alkali corrosion kinetics of Si_3N_4 from 950 to 1050°C were also examined in the same atmosphere (0.63 vol% alkali vapors). The reaction thickness of Si_3N_4 appears to vary linearly with the reaction time from 950 to 1050°C, suggesting that the alkali corrosion process is controlled by the oxidation of Si_3N_4 . At 1050°C, the alkali-enhanced oxidation of Si_3N_4 is approximately 10^7 times faster than the oxidation of Si_3N_4 in dry oxygen. Compared to SiC corroded in the same alkali atmosphere, Si_3N_4 seems to be less alkali-resistant than SiC.

The phase relations of the $\text{Na}_2\text{O}-\text{Al}_2\text{TiO}_5$ vertical section from 5-40 wt% Na_2O and 840-1100°C were studied. Phase analysis indicates that the $\text{Na}_2\text{O}-\text{Al}_2\text{TiO}_5$ section is not a true binary system. A tentative phase diagram for the $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{TiO}_2$ system was constructed based on the preliminary data.

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. Alkali Reaction Products

The soda-aluminum titanate phase relations were investigated in the region from 0-40 wt% soda and from 840-1100°C. The aluminum titanate was prepared by mixing the appropriate amounts of aluminum tri-sec butoxide and titanium butoxide using sol-gel techniques. The mixture was dried and fired at successively higher temperatures up to 1350°C, followed by x-ray diffraction analysis of the powders after each firing. After the 1350°C firing, the aluminum titanate was the only phase indicated by the diffraction pattern. Samples used for the alkali reaction study were prepared by repeatedly grinding

and mixing appropriate amounts of sodium carbonate and aluminum titanate 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 1100°C. The tubes were weighed before and after the heat treatments and there was no weight loss during the reaction. The phases formed after the heat treatments and the phase transition temperatures of the soda-aluminum titanate system 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-aluminum titanate reaction products at different temperatures. Based on the phase analysis for the compositions studied, a tentative phase diagram for the $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{TiO}_2$ system was constructed as shown in Figure 1. There appeared to be an unknown ternary phase in the ternary system which persisted after repeated grinding and firing at 900°C. The phase assemblage indicated that the $\text{Na}_2\text{O}-\text{Al}_2\text{TiO}_5$ section is not a true binary system, since the observed phases can not be expressed in terms of the end members (Na_2O and Al_2TiO_5). The phase assemblages for compositions outside the $\text{Na}_2\text{O}-\text{Al}_2\text{TiO}_5$ vertical section are being studied to verify the compatibility triangles shown in the $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{TiO}_2$ system.

II. Alkali Corrosion Kinetics

The alkali corrosion kinetics of Si_3N_4 (Kyocera) were examined in a constant alkali vapor concentration from 950 to 1050°C. The Si_3N_4 specimens were manufactured using hot isostatic pressing (HIP) and sialon as sintering aid. The system used to conduct the alkali corrosion tests, which has been described in previous reports, is shown in Figure 2. The boats containing the sodium nitrate salt were weighed before and after each run to determine the amount of weight loss of the sodium nitrate during the corrosion time interval. Figure 3 shows the weight loss of the salt as a function of time at 715°C. The weight loss data follow a linear trend, indicating a constant alkali concentration throughout the reaction. The slope gives a linear weight loss of 0.254 g sodium nitrate per hour. Using data from the weight loss and the flow rate of the compressed air, the alkali vapor concentration was calculated to be approximately 0.63 vol%.

The Si_3N_4 pellets were placed on an alumina holder and the gas flow was perpendicular to the measured pellet dimension. Alumina powder was used to protect the back of the pellets from reaction so that the reaction proceeded from one direction only. The thickness change of the Si_3N_4 pellets exposed to the alkali containing atmosphere was measured as described in previous reports. The reaction thickness of Si_3N_4 at 950, 1000, and 1050°C is plotted as a function of time, as shown in Figures 4, 5, and 6, respectively. The data appeared to be linear with time, suggesting a reaction rate controlled process. At 1050°C, the alkali-enhanced oxidation of Si_3N_4 is approximately 10^7 times faster than the oxidation of Si_3N_4 in dry oxygen. The reaction

rate at 1100°C is currently being measured and the analysis of the corrosion kinetics will be included in the next report upon the completion of the 1100°C run.

Figure 7 shows the SEM micrographs of the fracture surface of the as received specimen and the surface of the Si_3N_4 after a 19 h exposure at 1000°C in the alkali containing atmosphere. The grain boundaries appear to be preferentially attacked as evidenced by the well etched grains shown in the micrograph. This preferential attack may be caused by the segregation of the sintering aid at grain boundaries. The morphology of the grains does not appear to have been affected by the alkali exposure.

Table 1. Phase Analysis of the Soda-Aluminum Titanate System

Composition (wt%)		Temperature (°C)/ Time (h)	Observed Phases	Melting Temperature
Al ₂ TiO ₅	Soda			
95	5	840 / 300	NA ₅ T ₄ + TiO ₂ (tr) + un	-----
		900 / 200	NA ₅ T ₄ + TiO ₂ (tr) + un	
		1000 / 100	NA ₅ T ₄ + TiO ₂ (tr) + un	
		1100 / 100	NA ₅ T ₄ + TiO ₂ (tr) + un	
90	10	840 / 300	NA (tr) + NT ₃ (tr) + un	1048
		900 / 200	NA (tr) + NT ₃ (tr) + un	
		1000 / 100	NA ₁₁ + un	
		1100 / 100	NA ₁₁ + Liq	
85	15	840 / 300	NA + NT ₃ + un	1000
		900 / 200	NA + NT ₃ + un	
		1000 / 100	NA + Liq	
		1100 / 100	NA ₁₁ + Liq	
80	20	840 / 300	NA + NT ₃ + un	993
		900 / 200	NA + NT ₃ + un	
		1000 / 100	NA + Liq	
		1100 / 100	NA ₁₁ + NA + Liq	
70	30	840 / 300	NA + NT ₃ + un (tr)	1026
		900 / 200	NA + NT ₃ + un (tr)	
		1000 / 100	NA + un	
		1100 / 100	NA + Liq	
60	40	840 / 300	NA + N ₄ T ₅ + un	966
		900 / 200	NA + N ₄ T ₅ + un	
		1000 / 100	NA + Liq	
		1100 / 100	NA + Liq	

NA = NaAlO₂, NA₁₁ = NaAl₁₁O₁₇, NT₃ = Na₂Ti₃O₇, NA₅T₄ = NaAl₅Ti₂O₁₂,
N₄T₅ = Na₈Ti₅O₁₄, un = unknown single phase, Liq = liquid

Figure 1. Tentative phase diagram for the $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{TiO}_2$ system
(dashed circle represents unknown phase)

Figure 2. Schematic of alkali corrosion apparatus

Figure 3. Weight loss of sodium nitrate versus time

Figure 4. Thickness change versus time at 950°C for 0.63 vol% alkali

Figure 5. Thickness change versus time at 1000°C for 0.63 vol% alkali

Figure 6. Thickness change versus time at 1050°C for 0.63 vol% alkali

a.)

b.)

Figure 7. SEM micrographs of a.) fracture surface of as-received Si_3N_4
b.) Si_3N_4 after 19 h at 1000°C , glass etched away

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