Corrosion of Mullite by Molten Salts

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The interaction of molten salts of different Na₂O activities and mullite is examined with furnace and burner tests. The more-acidic molten salts form small amounts of Al₂O₃; the more-basic molten salts form various Na₂O·Al₂O₃·SiO₂ compounds. The results are interpreted using the Na₂O·Al₂O₃·SiO₂ ternary phase diagram, and some possible diffusion paths are discussed. The generally higher melting points of Na₂O·Al₂O₃·SiO₂ compounds lead to better behavior of mullite in molten salts, as compared to SiO₂-protected ceramics such as SiC. Mullite-coated SiC is discussed, and the corrosion behavior is evaluated.

I. Introduction

The corrosive action of molten salts is a well-known problem for components in combustion environments. Metallic alloys, as well as silicon-based ceramics, are susceptible to this type of corrosion. In the latter case, the process occurs by dissolution of the protective silica (SiO₂) scale to form a nonprotective liquid silicate:

\[ 2\text{SiO}_2(s) + \text{Na}_2\text{O}(s) \rightarrow \text{Na}_2\text{O}·2\text{SiO}_2(l) \]  
(1)

The introduction of alumina to the protective oxide scale leads to higher-melting Na₂O·Al₂O₃·SiO₂ compounds and may provide significantly better corrosion resistance.

This consideration has led us and other investigators to consider mullite as a protective coating on silicon carbide (SiC). This coating system is attractive, because mullite has a coefficient of thermal expansion that is remarkably similar to that of SiC. The purpose of this paper is to examine the interaction of mullite and mullite-coated SiC with Na₂O at various chemical activities.

This system is best understood with the aid of the Na₂O·Al₂O₃·SiO₂ phase diagram. An isothermal section at 1000°C is shown in Fig. 1. The major phases are silica, sodium silicates, mullite, corundum, nepheline (Na₂O·Al₂O₃·2SiO₂), and albite (Na₂O·Al₂O₃·6SiO₂). There also is a high-temperature form of nepheline—carnegieite. However, this should not form at the lower temperatures considered here. Also, many of these phases exist as solid solutions. Mullite and albite exist over a small solid-solution range, and nepheline exists over a larger range. These are shown as tick marks on the composition joins.

There is much information on the corrosion of refractory aluminosilicate compounds by sodium and potassium salts. These studies focus on such applications as glassmelting furnaces and coal gasifiers. Typically, these studies involve large amounts of Na₂O and K₂O at temperatures of 1000°C–1500°C.

![Fig. 1. Isothermal section for T = 1000°C of the Na₂O·Al₂O₃·SiO₂ ternary. Crosshatched areas indicate solid-solution ranges.](https://ntrs.nasa.gov/search.jsp?R=19970019643)
II. Thermodynamic Considerations

The critical issue in these experiments is the thermodynamic activity of Na2O, \( a_{Na_2O} \). A high activity of Na2O is termed a basic molten salt, and a low activity of Na2O is termed an acidic molten salt. This Na2O activity can be set by using thin films of Na2CO3 and Na2SO4 and an overpressure of CO2(g) or SO3(g), respectively:

\[
\begin{align*}
\text{Na}_2\text{CO}_3(l) & \rightleftharpoons \text{Na}_2\text{O}(s, l) + \text{CO}_2(g) \quad \left(a_{\text{Na}_2\text{O}} = \frac{K_3}{P_{\text{CO}_2}} = 8.06 \times 10^{-7}/P_{\text{CO}_2} \text{ at } 1000^\circ\text{C}\right) \quad (3) \\
\text{Na}_2\text{SO}_4(l) & \rightleftharpoons \text{Na}_2\text{O}(s, l) + \text{SO}_3(g) \quad \left(a_{\text{Na}_2\text{O}} = \frac{K_4}{P_{\text{SO}_3}} = 4.06 \times 10^{-16}/P_{\text{SO}_3} \text{ at } 1000^\circ\text{C}\right) \quad (4)
\end{align*}
\]

\( K_3 \) and \( K_4 \) are the equilibrium constants for reactions (3) and (4), respectively, and have been calculated from the thermochemical tables.\(^{13} \) The chemical activity of Na2CO3 and Na2SO4 are taken as unity, because these are essentially pure phases. However, Na2CO3 still decomposes to a greater extent than Na2SO4 and forms a more basic salt.

The dashed line in Fig. 1 represents the addition of Na2O to mullite. Movement toward pure Na2O represents increasing the activity of Na2O through a series of compatibility triangles, labeled as 1, 2, 3, and 4 in Fig. 1. The Na2O activity in each triangle was determined from the following equilibria:

\[
\begin{align*}
\text{Na}_2\text{O} + 3(3\text{Al}_2\text{O}_3'2\text{SiO}_2) & \rightleftharpoons \text{Na}_2\text{O}':\text{Al}_2\text{O}_3'6\text{SiO}_2 + 8\text{Al}_2\text{O}_3 \\
\text{Na}_2\text{O}_2'3\text{Al}_2\text{O}_3'4\text{SiO}_2 & \rightleftharpoons \text{Na}_2\text{O}_2'3\text{Al}_2\text{O}_3'4\text{SiO}_2
\end{align*}
\]

Table II. Summary of Experimental Conditions, Phases Predicted from an Ideal Diffusion Path, and Phases Observed

<table>
<thead>
<tr>
<th>Condition*</th>
<th>Description of experimental condition</th>
<th>Calculated partial pressure (bar)</th>
<th>Calculated activity of Na2O, ( a_{Na_2O} )</th>
<th>Predicted phases</th>
<th>Observed phases</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Furnace; Na2SO4/930 ppmv SO2-O2 atmosphere, 1000°C, 24 h</td>
<td>( 8.1 \times 10^{-4} )</td>
<td>( 1.2 \times 10^{-4} )</td>
<td>( 3.6 \times 10^{-12} )</td>
<td>Mullite, Al2O3, Na2SO4</td>
</tr>
<tr>
<td>B</td>
<td>Furnace; Na2SO4/1.56 ppmv SO2-O2 atmosphere, 1000°C, 24 h</td>
<td>( 1.0 \times 10^{-3} )</td>
<td>( 1.5 \times 10^{-4} )</td>
<td>( 2.7 \times 10^{-10} )</td>
<td>Mullite, Al2O3, Na2O2'3Al2O3'6SiO2, Na2O2'3Al2O3'2SiO2, Na2SO4</td>
</tr>
<tr>
<td>C</td>
<td>Furnace; Na2SO4/1.56 ppmv SO2-O2 atmosphere, 1000°C, 24 h</td>
<td>( 1.1 \times 10^{-5} )</td>
<td>( 8.7 \times 10^{-7} )</td>
<td>( 1.8 \times 10^{-8} )</td>
<td>Mullite, Al2O3, Na2O2'3Al2O3'6SiO2, Na2O2'3Al2O3'2SiO2, Na2SO4, NaAl2O4</td>
</tr>
<tr>
<td>D</td>
<td>Furnace; Na2CO3/1 bar CO2 atmosphere, 1000°C, 24 h</td>
<td>( 8.1 \times 10^{-7} )</td>
<td>( 4.0 \times 10^{-6} )</td>
<td>( 1.0 \times 10^{-10} )</td>
<td>Mullite, Al2O3, Na2O2'3Al2O3'6SiO2, Na2O2'3Al2O3'2SiO2, Na2SO4</td>
</tr>
<tr>
<td>E</td>
<td>Burner; 2 ppmw sodium, 0.05% sulfur in fuel, fuel:air = 0.025, 1000°C, 4 bar, 40 h</td>
<td>( 2.7 \times 10^{-3} )</td>
<td>( 4.0 \times 10^{-6} )</td>
<td>( 1.0 \times 10^{-10} )</td>
<td>Mullite, Al2O3, Na2O2'3Al2O3'6SiO2, Na2O2'3Al2O3'2SiO2, Na2SO4</td>
</tr>
</tbody>
</table>

Table I. Composition of Bulk Mullite

<table>
<thead>
<tr>
<th>Element</th>
<th>Amount (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum</td>
<td>30.6</td>
</tr>
<tr>
<td>Calcium</td>
<td>0.03</td>
</tr>
<tr>
<td>Copper</td>
<td>0.01</td>
</tr>
<tr>
<td>Iron</td>
<td>0.3</td>
</tr>
<tr>
<td>Sodium</td>
<td>0.06</td>
</tr>
<tr>
<td>Oxygen</td>
<td>bal.</td>
</tr>
<tr>
<td>Lead</td>
<td>0.8</td>
</tr>
<tr>
<td>Silicon</td>
<td>15.9</td>
</tr>
<tr>
<td>Titanium</td>
<td>0.07</td>
</tr>
<tr>
<td>Yttrium</td>
<td>0.03</td>
</tr>
<tr>
<td>Zinc</td>
<td>0.01</td>
</tr>
<tr>
<td>Zirconium</td>
<td>0.4</td>
</tr>
</tbody>
</table>

*Conditions A-E are for bulk mullite; condition F is for SiC and mullite-coated SiC.
regard this system as a diffusion couple of Na₂O and mullite. There are many detailed studies of analogous metallurgical systems. The three oxides—Na₂O, Al₂O₃, and SiO₂—are the three components of this system. If temperature, pressure, and composition are fixed, the phase rule then indicates that two-phase regions are possible in the product layer between the Na₂O and mullite. From the composition of these regions, delineation of some diffusion paths should be possible. Complications arise from the unknown identity of the diffusing species and extensive solid-solution formation in this system.

III. Experimental Procedure

The bulk mullite specimens were sintered from a powder made by a coprecipitation method (Tosoh Soda Co., Tokyo, Japan). A typical atomic emission analysis is shown in Table I. Coupons were cut to ~2.0 cm × 0.4 cm × 0.3 cm and ground with 15 μm diamond. One piece was polished further to a 1 μm finish with diamond paste and examined with the scanning electron microscope (SEM). There was no evidence of a second phase.

In addition, some mullite-coated SiC was examined. Sintered α-SiC with carbon and boron additives (Carborundum Co., Niagara Falls, NY) was used as the substrate of the same approximate dimension given above and coated on all six faces. The plasma-spray process used to deposit the mullite coating has been described in previous publications. It was shown that a thermal-shock-resistant coating can be applied by heating the substrate to ensure that the mullite retains its crystallinity.

Both the bulk and coated specimens were exposed to corrosive atmospheres in a laboratory furnace and a jet-fuel burner. These techniques have been described elsewhere. Briefly, heated coupons were air-brushed with an aqueous solution of Na₂SO₄ or Na₂CO₃. After the solution dried on the coupons, a film of salt remained. Dry salt loadings of 2-3 mg/cm² were used for all coupons. Two to four coupons were examined for each condition. The coupons then were placed in a laboratory furnace with a fixed gas atmosphere at 1000°C or 1089°C, which set the activity of Na₂O as shown in reactions (3) and (4) above. A free-energy minimization computer code was used to calculate the values of equilibrium $P_{SO₂}, P_{CO₂}$, and $a_{Na₂O}$ for our furnace exposures; the inputs were the salt and gas atmosphere. The experimental conditions are summarized in Table II.
thick conductive coating allowed electron optic examination and analysis through the entire thickness of the corrosion product. The sections were examined with an SEM equipped for energy-dispersive spectroscopy (EDS) and electron probe microanalysis (EPMA). For the EPMA measurements, the aluminum standard was Al₂O₃, the silicon standard was SiO₂, the sodium standard was NaF, and the oxygen standard was MgO.

IV. Results and Discussion

(1) Furnace Studies

Table II lists the predicted phases and observed products. Each of these experiments will be discussed, beginning with the most-acidic salt.

Condition A is the most-acidic salt, with $a_{\text{Na}_2\text{O}} = 3.6 \times 10^{-12}$.

XRD results indicated the presence of mullite, Na₂SO₄, and a small amount of Al₂O₃. A surface examination of the specimen in conjunction with EDS indicated an outer layer of condensed liquid Na₂SO₄, which is an effective source of Na₂O. The Na₂SO₄ was removed by dissolution in boiling water, revealing a rough surface with some degree of etching. XRD of this surface indicated only mullite. Apparently, the water-soluble layer contained Na₂SO₄ and Al₂O₃ (very likely as small particles).

From Fig. 2, the first three-phase region—mullite/alumina/albite—occurs when $a_{\text{Na}_2\text{O}} = 7.5 \times 10^{-12}$. The experimental conditions are less than this, so that only mullite and alumina are expected, as shown in Table II. These two phases have been observed experimentally. A proposed diffusion path is shown in Fig. 3, with the two-phase region between mullite and alumina enlarged to some solubility of Na₂O.

The burner conditions also have been described previously. These consist of a 4 atm (~0.4 MPa) pressurized burner using Jet A fuel. Salt was added as NaCl, which reacts with sulfur impurities in the fuel to form a Na₂SO₄ deposit. This type of situation simulates the actual corrosion process that occurs in a heat engine. Using the NASA Chemical Equilibrium Code, estimation of the $p_{\text{SO}_2}$ generated in such a burner (2 ppm sodium, 0.05% sulfur, Jet A fuel) and then calculation of the activity of Na₂O was possible. This information is given in Table II.

After exposure to these environments, the specimens were cooled and analyzed via several techniques. X-ray diffraction (XRD) was used to identify the crystalline phases. Even though there are many Na₂O-SiO₂-Al₂O₃ compounds in the XRD card files, there was not always a clear match of our XRD scans to those on file. In addition, glasses may form from some of these compounds and would not be identifiable by XRD. Elemental analysis was helpful in these cases. Polished cross sections were prepared by sputter-coating samples with gold and then electroplating with a few millimeters of nickel or copper. Then, the sample was polished with diamond paste using ethylene glycol as a lubricant to preserve the water-soluble phases.

Fig. 6. Inferred cross-sectional structure of sample shown in Fig. 4.

Fig. 7. Probable diffusion path for reaction examined in Fig. 4.
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Decreasing the amount of SO₂ to 11.56 ppm at 1000°C decreased the amount of SO₃ and then, according to Eq. (4), increased $a_{Na_2O}$. This is condition B in Table II, with $a_{Na_2O} = 2.9 \times 10^{-10}$. In this case, XRD showed mullite, Al₂O₃, Na₂SO₄, and a very small amount of Na₂O·Al₂O₃·2SiO₂. No Na₂O·Al₂O₃·6SiO₂ was detected. A polished cross section and associated X-ray dot maps are shown in Fig. 4. The corrosion-affected zone did not form a continuous product layer but rather a number of discontinuous regions 10–25 μm thick, with the corrosion-affected zone separated from the bulk by the predominately Na₂SO₄ melt. Na₂SO₄ may initially attack the grain boundaries of the mullite, and then the melt may surround the grains or collections of grains. The grain size of the mullite was several micrometers, which is consistent with intergranular attack in Fig. 4.

To reveal more information about these corrosion products, the surfaces were examined in the SEM before and after a boiling-water treatment. This is shown in Fig. 5. Before the boiling-water treatment, the surface primarily was solidified Na₂SO₄, as indicated by EDS analysis and XRD. After treatment in boiling water, the diffraction peaks for Na₂SO₄, Al₂O₃, and Na₂O·Al₂O₃·2SiO₂ disappeared, leaving only mullite peaks. Apparently, the melt that surrounded the mullite grains in Fig. 4 contained Na₂SO₄, Al₂O₃, and Na₂O·Al₂O₃·2SiO₂, which again was an effective source of Na₂O. The limits of resolution of our microprobe did not allow us to distinguish these products.

A proposed cross-sectional structure from the outer melt layer to the mullite is shown schematically in Fig. 6. Figure 7 shows a probable diffusion path; this is idealized, because the...
routes are shown along joins. Initially, some of the SiO
from
the
mullite
is
attacked
by
Na2O,
leaving
Al2O3. The initial removal of SiO2 is consistent with the refractory corrosion studies of Rigby and Hutton,12 and Fig. 3 shows it as the diffusion path from the mullite to the pure Al2O3. By moving down to this region, the diffusion path can bypass the mullite/alumina/albite and alumina/albite/nepheline compatibility triangles and move directly to the alumina/nepheline two-phase region. Some kinetic barrier to forming albite seems to exist, which is consistent with the refractory corrosion literature, as discussed in the Introduction. The primary product between the mullite and Na2O then is a two-phase mixture of Al2O3 and Na2O·Al2O3·2SiO2.

For condition C in Table II, the activity of Na2O was altered by increasing the temperature to 1089°C and keeping the amount of SO2 at 11.56 ppm, which leads to an aNa2O value of 1.3 × 10−8. XRD now showed Na2SO4, mullite, oriented Al2O3, and 3Na2O·2Al2O3·4SiO2, which is analogous to the situation described above, but with a slightly different sodium aluminosilicate composition.

Condition D in Table II is a more-basic molten salt—Na2CO3 in 1 atm CO2. After only ~5 min, the Na2CO3 layer was not detectable anymore. This indicated that Na2O completely reacted with the mullite, and instead of a diffusion-couple situation, a condensed phase reaction of Na2O and mullite existed. After 24 h of reaction, a product layer ~15 μm thick formed. A polished cross section and associated qualitative microprobe trace is shown in Fig. 8. The estimated error in the elemental analysis was ±1.5%, primarily because of the porosity of the mullite. Converting the data to moles of the individual components form indicated that the product layer was 1.2Na2O·1.5Al2O3·1SiO2. XRD showed the best match with the compound Na2O·Al2O3·SiO2, in reasonable agreement with the EPMA data.

The layer of sodium aluminosilicate has uniform composition. When this layer reaches the mullite, there is a concentration decrease in the ratio of sodium to mullite. There may be some penetration of the mullite by sodium, which is expected because mullite can transport sodium cations.19,20

(2) Burner Studies

An actual corrosion situation is a hot flame seeded with salt that reacts with sulfur fuel impurities, leading to Na2SO4 deposits on the components. As discussed, this is best simulated...
with a burner. Despite the complexity of a burner, determination of some basic chemical parameters and performance of an analysis similar to that conducted for the furnace are possible. As indicated in Table II, this produced an acidic salt deposit with \( a_{\text{Na}_2\text{SO}_4} = 1.0 \times 10^{-10} \). Results were similar to the furnace tests with acidic salts.

A polished cross section is shown in Fig. 9, which clearly shows a layer of \( \text{Na}_2\text{SO}_4 \) on mullite, as indicated by the sulfur elemental dot map. There was no evidence of reaction, and, unlike the furnace situation, \( \text{Al}_2\text{O}_3 \) was not detected in XRD. \( \text{Al}_2\text{O}_3 \) may have formed only in very small quantities.

A polished cross section of mullite-coated \( \text{SiC} \) after burner treatment, shown in Fig. 10(b), is compared to a coupon of uncoated \( \text{SiC} \) after a similar treatment, test condition F in Table II, is shown in Fig. 10(a); there was no evidence of reaction, and, an examination of the mullite surface shows no evidence of reaction; only a small amount of \( \text{Na}_2\text{SO}_4 \) has deposited in the asperities.

There seems to be no reaction in this case. However, \( \text{Na}_2\text{O} \) eventually will diffuse through the mullite and reach the \( \text{Na}_2\text{SO}_4 \) has deposited in the asperities. This is compared to a coupon of uncoated \( \text{SiC} \) after a similar treatment, test condition F in Table II, is shown in Fig. 10(a); there was no evidence of reaction, and, an examination of the mullite surface shows no evidence of reaction; only a small amount of \( \text{Na}_2\text{SO}_4 \) has deposited in the asperities.

There seems to be no reaction in this case. However, \( \text{Na}_2\text{O} \) eventually will diffuse through the mullite and reach the mullite/\( \text{SiC} \) interface. Figure 11 shows the mullite/\( \text{SiC} \) interface and an associated EDS trace, which indicates the presence of sodium. As mentioned earlier, mullite is well-known to be a good conductor for sodium.\(^{8,20}\) There are two driving forces for sodium diffusion through mullite: the activity gradient in sodium and sodium silicate formation. After long-term exposure, a liquid sodium silicate very likely will form at the mullite/\( \text{SiC} \) interface, which may lead to coating spallation. For long-term operation in sodium-containing atmospheres, a mullite coating is only a partial solution. Additional coating layers, which are better barriers to sodium, are necessary.\(^{21}\)

V. Summary and Conclusions

The interaction of \( \text{Na}_2\text{O} \) with mullite and mullite-coated \( \text{SiC} \) has been examined. Mullite generally behaves better in \( \text{Na}_2\text{O} \)-containing environments than pure \( \text{SiO}_2 \) because of the formation of higher-melting \( \text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2 \) compounds. The actual products are explained in terms of the thermodynamics of the system and diffusion paths in the \( \text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2 \) ternary. The more-aggressive burner tests are generally consistent with the furnace tests. The improved corrosion resistance of mullite and close coefficient of thermal expansion match to that of \( \text{SiC} \) make it a suitable protective-coating material. Over short terms, it looks quite promising. However, for longer times or in a high-sodium environment, the transport of sodium through mullite is a likely problem.

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References
