REACIONS OF CALCIUM ORTHOSILICATE AND BARIUM ZIRCONATE WITH OXIDES AND SULFATES OF VARIOUS ELEMENTS

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SUMMARY

Calcium orthosilicate and barium zirconate are being evaluated as the insulating layer of thermal barrier coatings for air-cooled gas turbine components. Surface temperatures of such coatings might reach 1300°-1400° C in hot spot locations. Thus chemical stability of these compounds was studied at 1100° and 1300° C in the presence of some oxides and sulfates for times to 400 and 200 hours respectively. The oxides and sulfates studied represent some of the oxidation products of impurities found in either the combustion air, or the fuels as well as the elements in the bond coat alloys. These compounds are listed below in four groups, according to their reactivity with calcium orthosilicate (actual composition was 1.78 CaO·SiO₂) and barium zirconate.

Compounds that reacted with 2 CaO·SiO₂: Na₂O, BaO, MgO, CoO, Al₂O₃, Cr₂O₃, SiO₂*, P₂O₅ and V₂O₅.

Compounds that did not react with 2CaO·SiO₂: Na₂SO₄, K₂O, K₂SO₄, BaSO₄, Na₂S, ZnO and Fe₂O₃.

Compounds that reacted with BaZrO₃: Al₂O₃, Cr₂O₃, Fe₂O₃, SiO₂, P₂O₅ and V₂O₅.

Compounds that did not react with BaZrO₃: Na₂O, Na₂SO₄, K₂O, K₂SO₄, MgO, CaO, CoO and ZnO.

When comparing these results with data available for reactions between similar compounds and ZrO₂-8w/oY₂O₃ it can be noted that all three materials reacted with SiO₂, P₂O₅ and V₂O₅. Also, zirconia was susceptible to attack by alkali and alkaline earth metal oxides. Calcium orthosilicate and barium zirconate were not susceptible to such attack but reacted readily with Al₂O₃ and Cr₂O₃ which did not react with ZrO₂-8w/oY₂O₃.

INTRODUCTION

The yttria-stabilized zirconia thermal barrier coating (TBC) developed at the NASA Lewis Research Center (refs. 1 and 2) has shown significant improvement in adherence and spall resistance over earlier efforts in this area (refs. 3 to 6). However, it has been found that yttria-stabilized zirconia is susceptible to attack by a number of compounds that might exist as impurities in turbine combustion gases (ref. 7). This might not be a problem in the case of aircraft.

*The reaction of SiO₂ with 2CaO·SiO₂ was not studied in these experiments, but based on reference 11 a reaction would be expected to occur.
gas turbines, since they burn high purity kerosenes. However, even here one could expect some difficulties if such zirconia thermal barriers were used in a salt air (marine) environment. In non-aircraft gas turbines, burning dirtier fuels such as crude or residual fuel oils and possibly future synthetic fuels, the potential problems would be expected to be much worse. Indeed, very short lives were observed in burner rig tests of ZrO₂-12w/oY₂O₃/NiCrAlY thermal barriers exposed to combustion gases doped with 5 ppm Na and 2 ppm V (ref. 8). Analysis of these tests indicated that the worst condition occurred when the impurity condensed as a liquid (ref. 9). In the search for alternate coatings with improved resistance to corrosion, calcium orthosilicate and barium zirconate are being tested as potential materials for thermal barrier coatings. The former material has already been shown to offer a significant improvement over zirconia in resistance to sodium and vanadium-doped combustion gases (ref. 8). The present investigation supports this quest for improved coatings. Its specific purpose was to use laboratory tests to provide insight into the chemical stability of calcium orthosilicate and barium zirconate in the presence of potential fuel, air and bond coat derived impurities. The experiments were performed in furnaces at 1100° and 1300° C for times to 400 and 200 hours, respectively. The test temperatures reflect hot spot conditions for TBC coated components in current industrial gas turbines and TBC surface temperatures expected on larger areas in advanced gas turbines. As in the study of ZrO₂-8w/oY₂O₃ (Ref. 7), the phase compositions of the reaction products were determined by X-ray diffraction (XRD) analysis.

EXPERIMENTAL PROCEDURE

MATERIALS

The calcium orthosilicate used in this investigation was in the form of commercially available plasma spray powder (-200 +325 mesh). While the chemical analysis indicated that the calcium and silicon content in the material corresponded to a 1.78 CaO·SiO₂ composition, the XRD pattern taken with Cu Kα radiation revealed that this silicate was primarily a monoclinic form, called laurite or β-Ca₂SiO₄ (ref. 10). Some of the diffraction lines, due to the closeness of their spacings, were not resolved but recorded as one. For example the strong lines (200) and (022) or (013), (103) and (121) were observed as one diffraction line. Spectrographic analysis revealed the presence of the following impurities in weight percent or PPM (parts per million): 0.8% Al, 5 PPM Co, 60 PPM Cr, 100 PPM Cu, 410 PPM Fe, 0.2% Mg, 20 PPM Mn, 40 PPM Mo, 90 PPM Ni, 320 PPM Ti and 120 PPM Zr. Barium zirconate (BaZrO₃) was prepared by mixing high purity monoclinic ZrO₂ (particle size 1-5 microns) with reagent grade BaCO₃ powder and reacting the mixture for 100 hours at 1300°C in a platinum dish. These conditions were sufficient to complete the synthesis of BaZrO₃. The completion of the reaction was verified by XRD. All the diffraction lines were accounted for as belonging to BaZrO₃ (perovskite structure) except one weak line (d = 3.048Å), which could not be identified.

The following reagent grade compounds, representing impurities in the fuels and in the combustion air as well as the elements of the bond coat alloy were reacted with 2CaO·SiO₂ and BaZrO₃: Na₂O, Na₂SO₄, K₂O, K₂SO₄, CaO, BaO, BaSO₄, NiO, CoO, MgO, ZnO, Fe₂O₃, Al₂O₃, Cr₂O₃, SiO₂,
V_2O_5 and P_2O_5. For practical reasons Na_2O, K_2O, CaO, BaO and CoO were introduced in the form of their carbonates. Also (NH_4)_2HPO_4 was substituted for P_2O_5 to facilitate handling.

Preparation of the Specimens

Binary powder mixtures of 2CaO·SiO_2 or BaZrO_3 with the above listed compounds were prepared by thoroughly mixing, in a mortar, 1 gram of 2CaO·SiO_2 or BaZrO_3 with an "equivalent" amount of the compound. The "equivalent" amounts were calculated in the manner that for each atom of Ca or Ba there would be an atom of an element such as Na, Ni, Fe, etc. All mixtures were packed in small cylindrical containers made of 0.6 cm diameter platinum tubing with one end welded shut. After filling with the powder mixtures, the other end of each tube was pinched tightly.

Heat Treatment and XRD Analysis

One set of samples so prepared was heated at 1100°C for 200 hours, after which time a small amount of material was removed from each container for XRD analysis. The remainder of each sample in the set was heated at the same temperature for an additional 200 hours. Thus, we obtained samples which were heat treated for 200 and for 400 hours. Similarly the second set of samples was heated at 1300°C for 100 and 200 hours.

After each heat treatment, the samples were ground in a mortar and subjected to XRD analysis in a diffractometer equipped with a copper X-ray tube. During analysis of the data, attention was paid not only to the phases which were present, but also to the absence of certain phases. Mainly two publications were used as guides in the analysis: Powder Diffraction File Search Manual (ref. 10) and Phase Diagrams for Ceramists (ref. 11).

RESULTS

The results obtained in this investigation are shown below. The 2CaO·SiO_2 and BaZrO_3 systems are discussed separately.

Na_2O

There is a ternary equilibrium diagram for the Na_2O-CaO-SiO_2 system (ref. 11), however the zone connecting Na_2O and 2CaO·SiO_2 is uncharted. At 1100°C sodium oxide reacted with larnite. The extent of reaction increased with time. The detected phases were 2CaO·SiO_2 and Na_2O·CaO·SiO_2. After 100 hours at 1300°C the observed phases were also 2CaO·SiO_2 and Na_2O·CaO·SiO_2. However, after 200 hours a new unknown phase appeared and the amount of Na_2O·CaO·SiO_2 decreased substantially. This indicates that Na_2O·CaO·SiO_2 was unstable at this temperature.
The original mixture contained two compounds, namely $2\text{CaO} \cdot \text{SiO}_2$ and $\text{Na}_2\text{SO}_4$ (thenardite). After heat treatment at 1100° and 1300° C, thenardite disappeared and the presence of a new phase was observed. Based on previous results (ref. 7) this phase is some other form of sodium sulfate.

The existing equilibrium phase diagram in the $\text{K}_2\text{O}-\text{CaO}-\text{SiO}_2$ system is incomplete and does not cover the area connecting $\text{K}_2\text{O}-2\text{CaO} \cdot \text{SiO}_2$. XRD analysis of the sample after 200 hours at 1100° C revealed the presence of $2\text{CaO} \cdot \text{SiO}_2$ and of a few weak lines, that could not be accounted for. The diffraction lines produced by this sample are considerably weaker than those obtained from the unreacted sample. The same can be said about the sample, which was heat treated at 1100° C for 400 hours, except that XRD lines due to $2\text{CaO} \cdot \text{SiO}_2$ were much better defined. Similar results were obtained at 1300° C. No $\text{CaO} \cdot \text{K}_2\text{O} \cdot \text{SiO}_2$ or KOH were detected. Either the $\text{K}_2\text{O}$ did not react with $2\text{CaO} \cdot \text{SiO}_2$ and was lost by evaporation or a glassy phase formed, which could not be detected by XRD.

The XRD data obtained indicated that, at 1100° C, $\text{K}_2\text{SO}_4$ did not react with $2\text{CaO} \cdot \text{SiO}_2$. After heat treatment at 1300° C for 100 hours, the detected phases were $2\text{CaO} \cdot \text{SiO}_2$, $\text{K}_2\text{SO}_4$ and an unknown compound. Continued heat treatment reduced the amount of $\text{K}_2\text{SO}_4$. Because the intensities of diffractions lines produced by $2\text{CaO} \cdot \text{SiO}_2$ were not affected by the heat treatments, one can conclude that there was no reaction between $\text{K}_2\text{SO}_4$ and $2\text{CaO} \cdot \text{SiO}_2$. The observed unknown phase was probably some form of $\text{K}_2\text{SO}_4$.

According to the existing equilibrium phase diagram for $\text{BaO}-\text{CaO}-\text{SiO}_2$ system (ref. 11), barium oxide should react with larnite by forming barium silicate and calcium oxide. At both temperatures (1100° and 1300° C), the reaction was complete as no larnite XRD lines were detected. The predominant phase was a compound, the lines of which could be indexed in a manner similar to $(\text{Ba}_{1.55} \text{Ca}_{0.45}) \cdot \text{SiO}_4$. It is reasonable to assume that this compound represents compounds with the general formula $2(\text{Ca}_x\text{Ba}_{1-x}) \cdot \text{SiO}_2$. The few unindexed lines were weak and could not be related to $2\text{BaO} \cdot \text{SiO}_2$, $\text{CaO}$, etc.

No reaction between $2\text{CaO} \cdot \text{SiO}_2$ and $\text{BaSO}_4$ was observed.

According to the existing equilibrium diagram for the $\text{CaO}-\text{MgO}-\text{SiO}_2$ system, MgO should react with $2\text{CaO} \cdot \text{SiO}_2$ to form certain amounts of $3\text{CaO} \cdot \text{MgO} \cdot \text{SiO}_2$ (merwinite). The phases observed after heat treatment at 1100° C were MgO,
2CaO·SiO₂ and an unknown compound, isomorphic with (2CaO·SiO₂)₅.₆
(3CaO·MgO·2SiO₂)₄.₄ (ref. 10). The heat treatment at 1300°C caused dis-
appearance of 2CaO·SiO₂; the remaining phases being the unknown compound and
MgO.

NiO

Nickel oxide did not react with larnite at 1100°C nor at 1300°C. This
observation is in agreement with the tentative CaO-NiO-SiO₂ equilibrium dia-
gram (ref. 11).

CoO

The ternary CaO-CoO-SiO₂ equilibrium diagram is not available. Very
little reaction occurred at 1100°C and only a trace of an unknown phase was
detected by x-ray. The main phases were 2CaO·SiO₂ and CoO. At 1300°C the
reaction advanced to the point where the predominant phases were CoO and an un-
known compound. The strongest XRD-lines of larnite were only detected as a weak
line. Thus, it can be stated that CoO reacted with 2CaO·SiO₂.

ZnO

An equilibrium diagram for the ZnO-CaO-SiO₂ systems exists (ref. 11). In
agreement with the diagram, the experimental data indicated that ZnO did not
react with larnite at 1100°C nor 1300°C. The samples, heat treated at both
temperatures, produced well defined XRD patterns of 2CaO·SiO₂ and ZnO.

Fe₂O₃

At 1100°C no reaction was detected between larnite and Fe₂O₃ (hem-
atite). After heat treatment at 1300°C, the detected phases were larnite, hematite and an unknown compound. According to the existing equilibrium dia-
gram (ref. 11), no reaction should take place between these two compounds.

Al₂O₃

At 1100°C and 1300°C, alumina reacted completely with larnite. No free
alumina was observed. The detected phases were 2CaO·Al₂O₃·SiO₂ and
2CaO·SiO₂ which is in agreement with the existing equilibrium phase diagram
(ref. 11).

Cr₂O₃

At 1100°C, Cr₂O₃ reacted with larnite to give 3CaO·Cr₂O₃·3SiO₂
(uvarovite). No Cr₂O₃ was detected. However, at 1300°C no uvarovite was
detected. Only the original compounds, 2CaO·SiO₂ and Cr₂O₃ were ob-
served. This is consistent with the equilibrium diagram (ref. 11). If the ex-
periment were performed at 1300°C only, one could draw a logical conclusion
that Cr₂O₃ did not react with larnite. However, the data obtained at
1100°C suggest that during the heat-up period to 1300°C, Cr₂O₃ reacted
with $2\text{CaO} \cdot \text{SiO}_2$ to form uvarovite which later decomposed at the higher temperature into the two original compounds.

$\text{P}_2\text{O}_5$

According to the existing equilibrium diagram (ref. 11) the reaction products should have been $3\text{CaO} \cdot \text{P}_2\text{O}_5$, $\text{CaO} \cdot \text{SiO}_2$ and $\text{SiO}_2$ ($\alpha$-cristobalite). However, after heat treatment at $1100^\circ\text{C}$, the diffraction lines of one or two unknown compounds were detected. The reaction at $1300^\circ\text{C}$ produced $3\text{CaO} \cdot \text{P}_2\text{O}_5$ (calcium orthophosphate) and an unknown compound with an XRD pattern different from the one observed at $1100^\circ\text{C}$. It was difficult to establish the presence or absence of $\alpha$-cristobalite because its diffraction lines were coincident with the lines of the unknown compound or compounds.

$\text{V}_2\text{O}_5$

Experiments at $1100^\circ\text{C}$ revealed that $\text{V}_2\text{O}_5$ (vanadium pentoxide) reacted with larnite to form an unknown compound. Some unreacted $\text{V}_2\text{O}_5$ was also found to be present. No larnite was detected. During experiments at $1300^\circ\text{C}$, the sample crept out of the platinum container and consequently no analysis was performed. Thus, it is reasonable to assume that $\text{V}_2\text{O}_5$ reacted at $1300^\circ\text{C}$ with $2\text{CaO} \cdot \text{SiO}_2$.

$\text{BaZrO}_3$

$\text{Na}_2\text{O}$

Apparently there was no reaction between $\text{Na}_2\text{O}$ and $\text{BaZrO}_3$. XRD patterns obtained from the samples heat treated at $1100^\circ\text{C}$ and $1300^\circ\text{C}$ revealed strong, well defined lines of $\text{BaZrO}_3$ and a few weak lines of an unknown phase. No $\text{Na}_2\text{O}$, $\text{NaOH}$ or $\text{Na}_2\text{ZrO}_3$ were detected. Apparently most of $\text{Na}_2\text{O}$ was lost by evaporation.

$\text{Na}_2\text{SO}_4$

At both temperatures, $1100^\circ\text{C}$ and $1300^\circ\text{C}$, no reaction was observed. The samples gave a very strong $\text{BaZrO}_3$ pattern and some weak lines which did not correspond to $\text{Na}_2\text{SO}_4$ or any other known form of sodium sulfate. However, based on previous results (ref. 7), these lines can be attributed to an unindexed form of sodium sulfate.

$\text{K}_2\text{O}$

$\text{K}_2\text{O}$ did not react with $\text{BaZrO}_3$ at $1100^\circ\text{C}$ or $1300^\circ\text{C}$. No $\text{K}_2\text{O}$ was detected. The XRD pattern of $\text{BaZrO}_3$ remained unchanged. It is reasonable to assume that $\text{K}_2\text{O}$ was lost by evaporation.

$\text{K}_2\text{SO}_4$

As with $\text{Na}_2\text{SO}_4$, $\text{BaZrO}_3$ did not react with $\text{K}_2\text{SO}_4$. After heat treatments at $1100^\circ\text{C}$ and $1300^\circ\text{C}$, the observed phases were $\text{BaZrO}_3$ and some
K$_2$SO$_4$. It is of interest to point out that unlike Na$_2$SO$_4$, K$_2$SO$_4$ did not form any complex potassium sulfate.

**MgO**

MgO did not react with BaZrO$_3$.

**CaO**

No reaction was observed between CaO and BaZrO$_3$.Obviously, barium zirconate must be a more stable compound than calcium zirconate.

**NiO**

NiO did not react with BaZrO$_3$ at 1100º C or at 1300º C. The XRD patterns were rather deceptive because all NiO diffraction lines (except 311) coincided with those of BaZrO$_3$.

**CoO**

CoO did not react with BaZrO$_3$.

**ZnO**

No reaction was observed between ZnO and BaZrO$_3$.

**Fe$_2$O$_3$**

Analysis of the diffraction patterns of the samples reacted at 1100º and 1300º C revealed that Fe$_2$O$_3$ reacted with BaZrO$_3$. The detected phases were BaZrO$_3$, BaO·6Fe$_2$O$_3$ and monoclinic ZrO$_2$ (small amount). In addition the samples became black and magnetic. The black color and the magnetic property should be attributed to BaO·6Fe$_2$O$_3$ as BaZrO$_3$ and ZrO$_2$ have a light color and are not magnetic.

**Al$_2$O$_3$**

The obtained data indicated that Al$_2$O$_3$ readily reacted with BaZrO$_3$ at 1100º and 1300º C to form BaO·Al$_2$O$_3$. In addition to the above compound, the heat treated sample contained BaZrO$_3$ and monoclinic ZrO$_2$. No Al$_2$O$_3$ was detected. (However, in the presence of compounds containing heavy elements like Ba or Zr, small amounts of Al$_2$O$_3$ would not be detected.)

**Cr$_2$O$_3$**

At 1100º and 1300º C, Cr$_2$O$_3$ reacted with BaZrO$_3$ to form BaCrO$_4$. In this reaction, chromium changed its valency from 3 to 6. In addition to BaCrO$_4$, monoclinic ZrO$_2$ was detected. No BaZrO$_3$ or Cr$_2$O$_3$ were observed.
**SiO₂**

$\text{SiO}_2$ reacted with $\text{BaZrO}_3$ at $1100^\circ$ and $1300^\circ$ C. In accordance with the existing $\text{Ba}_6\text{Zr}_2\text{Si}_3\text{O}_{12}$ equilibrium phase diagram (ref. 11) the detected phases were $2\text{BaO} \cdot 2\text{ZrO}_2 \cdot 3\text{SiO}_2$ and $\text{BaZrO}_3$. It appears that the samples heat treated at $1100^\circ$ C might also contain a small amount of unreacted silica ($\alpha$-cristobalite).

**P₂O₅**

At both temperatures, $1100^\circ$ and $1300^\circ$ C, $\text{P}_2\text{O}_5$ reacted with $\text{BaZrO}_3$ to form $\text{BaO} \cdot \text{ZrO}_2 \cdot \text{P}_2\text{O}_5$. No $\text{BaZrO}_3$ was detected. There were a few XRD lines, some of them relatively strong, that could not be identified.

**V₂O₅**

$\text{V}_2\text{O}_5$ reacted readily with $\text{BaZrO}_3$ at $1100^\circ$ and $1300^\circ$ C. Even after only 200 hours at $1100^\circ$ C, all $\text{BaZrO}_3$ and $\text{V}_2\text{O}_5$ were consumed. The observed phases were $3\text{BaO} \cdot \text{V}_2\text{O}_5$, monoclinic $\text{ZrO}_2$ and an unknown compound.

**DISCUSSION**

The results obtained in this investigation are summarized in tables 1 and 2. These tables list all the chemical compounds used and the products of their reactions with calcium silicate and barium zirconate at $1100^\circ$ and $1300^\circ$ C. They also include columns marked with the letters "N" or "Y" indicating that essentially no reaction took place (N) or that, yes, there was a partial or complete reaction (Y). The entry "unknown phase" was used when some lines of an XRD pattern could not be attributed to any compound listed in the Powder Diffraction File Search Manual (ref. 10). In general the heat treatments at $1100^\circ$ and $1300^\circ$ C produced similar results. When reactions were observed, they were usually the same at both temperatures. If there was no reaction at $1100^\circ$, there was generally none at $1300^\circ$ C. It is noteworthy that no monovalent or divalent oxides and sulfates reacted with barium zirconate. Similarly, calcium orthosilicate was not affected by sulfates, however, it was attacked by sodium, barium and cobalt oxides. Vanadium and phosphorous are impurities generally contained in industrial fuels and their pentoxides reacted readily with both barium zirconate and calcium orthosilicate.

$\text{Al}_2\text{O}_3$ and $\text{Cr}_2\text{O}_3$, which are oxides of the component elements of the bond coat, reacted with both materials. This indicates that at very high oxide/bond coat interface temperatures, calcium orthosilicate and barium zirconate might not be compatible with $\text{MCrAlY}$ type bond coat oxidation products.

In order to compare the chemical stability of calcium orthosilicate and barium zirconate with yttria-stabilized zirconia under the same conditions, table 3 was prepared. It shows how the three thermal barrier materials behaved in the presence of the same impurities when exposed at $1300^\circ$ C for 200 hours. Because some of the reaction experiments were not performed, the information necessary to complete this table was obtained from reference 11. It can be seen
that 10 out of 17 impurities reacted or would have reacted with calcium orthosilicate and ZrO$_2$-8w/oY$_2$O$_3$ and 7 out of 17 reacted or would have reacted with barium zirconate. The impurities that reacted with all three materials were BaO, SiO$_2$, P$_2$O$_5$ and V$_2$O$_5$, whereas alkali metal sulfates did not react with any of them. The information obtained from this investigation should be of interest in the analysis and solution of problems encountered during the development and testing of thermal barrier coatings.

SUMMARY OF RESULTS

The chemical stability of calcium orthosilicate and barium zirconate were studied at 1100$^\circ$ and 1300$^\circ$ C in the presence of some oxides and sulfates for times to 400 and 200 hours, respectively. These oxides and sulfates represent some of the potential impurities that may be found in gas turbine combustion gases or that may be formed as oxidation products of the elements of bond coat alloys.

The impurities that reacted with 2CaO·SiO$_2$ are Na$_2$O, BaO, MgO, CoO, Al$_2$O$_3$, Cr$_2$O$_3$, P$_2$O$_5$ and V$_2$O$_5$.

The impurities that did not react with 2CaO·SiO$_2$ are Na$_2$SO$_4$, K$_2$O, K$_2$SO$_4$, BaSO$_4$, NiO, ZnO and Fe$_2$O$_3$.

The impurities that reacted with BaZrO$_3$ are Al$_2$O$_3$, Fe$_2$O$_3$, Cr$_2$O$_3$, SiO$_2$, P$_2$O$_5$ and V$_2$O$_5$.

The impurities that did not react with BaZrO$_3$ are Na$_2$O, Na$_2$SO$_4$, K$_2$O, K$_2$SO$_4$, MgO, CaO, CoO and ZnO.

As a result of this study and a previous study of reactions of potential impurities with ZrO$_2$ 8w/oY$_2$O$_3$ (7) it was noted that BaO, SiO$_2$, P$_2$O$_5$ and V$_2$O$_5$ react with all three materials after 200 hours at 1300$^\circ$ C and that alkali metal sulfates do not react.

REFERENCES


### TABLE I. SUMMARY OF REACTIONS BETWEEN CALCIUM ORTHOSILICATE AND OXIDES AND SULFATES OF VARIOUS ELEMENTS
(Y = REACTION WAS DETECTED; N = NO REACTION WAS OBSERVED)

<table>
<thead>
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<th>Temperature</th>
<th>1100° C</th>
<th>1300° C</th>
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<tbody>
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<td>Time</td>
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<td>400 hr</td>
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<tr>
<td>Na₂O</td>
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<td></td>
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<td>N</td>
</tr>
<tr>
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<td>2CaO·SiO₂</td>
<td>N</td>
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<td>2CaO·SiO₂</td>
<td>N</td>
</tr>
<tr>
<td></td>
<td>ZnO</td>
<td>Unknown phase</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>2CaO·SiO₂</td>
<td>N</td>
</tr>
<tr>
<td></td>
<td>Fe₂O₃</td>
<td>Unknown phase</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>2CaO·Al₂O₃·SiO₂</td>
<td>Y</td>
</tr>
<tr>
<td></td>
<td>2CaO·SiO₂</td>
<td>N</td>
</tr>
<tr>
<td>Cr₂O₅</td>
<td>3CaO·Cr₂O₅·SiO₂</td>
<td>Y</td>
</tr>
<tr>
<td></td>
<td>2CaO·SiO₂</td>
<td>Y</td>
</tr>
<tr>
<td></td>
<td>Cr₂O₅</td>
<td>Unknown phase</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>One or two unknown phases</td>
<td>Y</td>
</tr>
<tr>
<td></td>
<td>3CaO·P₂O₅</td>
<td>Y</td>
</tr>
<tr>
<td></td>
<td>trace of V₂O₅</td>
<td>Unknown phase</td>
</tr>
<tr>
<td>V₂O₅</td>
<td>Unknown phase</td>
<td>Sample lost</td>
</tr>
<tr>
<td>TABLE 2: SUMMARY OF REACTIONS BETWEEN BARIUM ZIRCONATE AND OXIDES AND SULFATE OF VARIOUS ELEMENTS (Y - REACTION WAS DETECTED; N - NO REACTION WAS OBSERVED)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>Temperature</td>
<td>1100°C</td>
<td></td>
</tr>
<tr>
<td>Time</td>
<td>200 hr</td>
<td>400 hr</td>
</tr>
<tr>
<td>Na₂O</td>
<td>BaZrO₃ unknown phase</td>
<td>N</td>
</tr>
<tr>
<td>Na₂SO₄</td>
<td>BaZrO₃ unknown phase</td>
<td>N</td>
</tr>
<tr>
<td>K₂O</td>
<td>BaZrO₃</td>
<td>N</td>
</tr>
<tr>
<td>K₂SO₄</td>
<td>BaZrO₃</td>
<td>N</td>
</tr>
<tr>
<td>MgO</td>
<td>BaZrO₃</td>
<td>N</td>
</tr>
<tr>
<td>CaO</td>
<td>BaZrO₃</td>
<td>N</td>
</tr>
<tr>
<td>NiO</td>
<td>BaZrO₃</td>
<td>N</td>
</tr>
<tr>
<td>CoO</td>
<td>BaZrO₃</td>
<td>N</td>
</tr>
<tr>
<td>ZnO</td>
<td>BaZrO₃</td>
<td>N</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>BaZrO₃</td>
<td>Y</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>BaZrO₃</td>
<td>Y</td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>BaCrO₄</td>
<td>Y</td>
</tr>
<tr>
<td>SiO₂</td>
<td>2BaO·2ZrO₂·3SiO₂</td>
<td>Y</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>BaO·ZrO₂·P₂O₅ unknown phase</td>
<td>Y</td>
</tr>
<tr>
<td>V₂O₅</td>
<td>3BaO·V₂O₅</td>
<td>Y</td>
</tr>
</tbody>
</table>
TABLE 3 - COMPARISON OF CHEMICAL REACTIONS BETWEEN ZrO<sub>2</sub> 8w/o Y<sub>2</sub>O<sub>3</sub>, 2CaO·SiO<sub>2</sub>, BaZrO<sub>3</sub> AND OXIDES AND SULFATES OF VARIOUS ELEMENTS AFTER 200 hr AT 1300°C
(Y = REACTION WAS DETECTED, N = NO REACTION WAS OBSERVED)

<table>
<thead>
<tr>
<th></th>
<th>ZrO&lt;sub&gt;2&lt;/sub&gt;-8w/o Y&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</th>
<th>2CaO·SiO&lt;sub&gt;2&lt;/sub&gt;</th>
<th>BaZrO&lt;sub&gt;3&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>Na&lt;sub&gt;2&lt;/sub&gt;ZrO&lt;sub&gt;3&lt;/sub&gt; cubic</td>
<td>2CaO·SiO&lt;sub&gt;2&lt;/sub&gt; unknown phase Na&lt;sub&gt;2&lt;/sub&gt;O·CaO·SiO&lt;sub&gt;2&lt;/sub&gt; (trace)</td>
<td>Y BaZrO&lt;sub&gt;3&lt;/sub&gt; unknown phase</td>
</tr>
<tr>
<td>Na&lt;sub&gt;2&lt;/sub&gt;SO&lt;sub&gt;4&lt;/sub&gt;</td>
<td>ZrO&lt;sub&gt;2&lt;/sub&gt; cubic unknown phase</td>
<td>2CaO·SiO&lt;sub&gt;2&lt;/sub&gt; unknown phase</td>
<td>N BaZrO&lt;sub&gt;3&lt;/sub&gt; unknown phase</td>
</tr>
<tr>
<td>K&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>ZrO&lt;sub&gt;2&lt;/sub&gt; monoclinic Y BaZrO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>2CaO·SiO&lt;sub&gt;2&lt;/sub&gt; unknown phase</td>
<td>N BaZrO&lt;sub&gt;3&lt;/sub&gt; unknown phase</td>
</tr>
<tr>
<td>K&lt;sub&gt;2&lt;/sub&gt;SO&lt;sub&gt;4&lt;/sub&gt;</td>
<td>ZrO&lt;sub&gt;2&lt;/sub&gt; cubic unknown phase</td>
<td>2CaO·SiO&lt;sub&gt;2&lt;/sub&gt; unknown phase K&lt;sub&gt;2&lt;/sub&gt;SO&lt;sub&gt;4&lt;/sub&gt; (trace)</td>
<td>N BaZrO&lt;sub&gt;3&lt;/sub&gt; unknown phase</td>
</tr>
<tr>
<td>BaO</td>
<td>BaZrO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>Y 2(Ca&lt;sub&gt;1-x&lt;/sub&gt;Ba&lt;sub&gt;x&lt;/sub&gt;)SiO&lt;sub&gt;2&lt;/sub&gt; CaO</td>
<td>Y Not tested</td>
</tr>
<tr>
<td>BaSO&lt;sub&gt;4&lt;/sub&gt;</td>
<td>Not tested</td>
<td>2CaO·SiO&lt;sub&gt;2&lt;/sub&gt; BaSO&lt;sub&gt;4&lt;/sub&gt;</td>
<td>N Not tested</td>
</tr>
<tr>
<td>MgO</td>
<td>ZrO&lt;sub&gt;2&lt;/sub&gt; cubic unknown phase MgO</td>
<td>MgO unknown phase</td>
<td>Y BaZrO&lt;sub&gt;3&lt;/sub&gt; unknown phase</td>
</tr>
<tr>
<td>CaO</td>
<td>CaZrO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>Y Not tested</td>
<td>Y BaZrO&lt;sub&gt;3&lt;/sub&gt; CaO</td>
</tr>
<tr>
<td>NiO</td>
<td>ZrO&lt;sub&gt;2&lt;/sub&gt; cubic unknown phase NiO</td>
<td>2CaO SiO&lt;sub&gt;2&lt;/sub&gt; NiO</td>
<td>N BaZrO&lt;sub&gt;3&lt;/sub&gt; NiO</td>
</tr>
<tr>
<td>CoO</td>
<td>Not tested</td>
<td>CoO unknown phase 2CaO·SiO&lt;sub&gt;2&lt;/sub&gt; (trace)</td>
<td>Y BaZrO&lt;sub&gt;3&lt;/sub&gt; CoO</td>
</tr>
<tr>
<td>ZnO</td>
<td>ZrO&lt;sub&gt;2&lt;/sub&gt; cubic unknown phase</td>
<td>2CaO·SiO&lt;sub&gt;2&lt;/sub&gt; ZnO</td>
<td>N BaZrO&lt;sub&gt;3&lt;/sub&gt; ZnO</td>
</tr>
<tr>
<td>Fe&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>ZrO&lt;sub&gt;2&lt;/sub&gt; cubic Fe&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>2CaO·SiO&lt;sub&gt;2&lt;/sub&gt; Fe&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt; unknown phase</td>
<td>N BaZrO&lt;sub&gt;3&lt;/sub&gt; BaO·6Fe&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt; ZrO&lt;sub&gt;2&lt;/sub&gt; (mon)</td>
</tr>
<tr>
<td>Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>ZrO&lt;sub&gt;2&lt;/sub&gt; cubic Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>2CaO·Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;·SiO&lt;sub&gt;2&lt;/sub&gt; 2CaO·SiO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>Y BaZrO&lt;sub&gt;3&lt;/sub&gt; BaO·Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt; ZrO&lt;sub&gt;2&lt;/sub&gt; (mon)</td>
</tr>
<tr>
<td>Cr&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>ZrO&lt;sub&gt;2&lt;/sub&gt; cubic Cr&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>2CaO·SiO&lt;sub&gt;2&lt;/sub&gt; Cr&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>Y BaCrO&lt;sub&gt;4&lt;/sub&gt; ZrO&lt;sub&gt;2&lt;/sub&gt; (mon) Cr&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
</tr>
<tr>
<td>SiO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>ZrO&lt;sub&gt;2&lt;/sub&gt; cubic SiO&lt;sub&gt;2&lt;/sub&gt; mon SiO&lt;sub&gt;2&lt;/sub&gt; SiO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>Not tested</td>
<td>Y 2BaO·ZrO&lt;sub&gt;2&lt;/sub&gt;·3SiO&lt;sub&gt;2&lt;/sub&gt; BaZrO&lt;sub&gt;3&lt;/sub&gt;</td>
</tr>
<tr>
<td>P&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;5&lt;/sub&gt;</td>
<td>ZrO&lt;sub&gt;2&lt;/sub&gt; mon ZrO&lt;sub&gt;2&lt;/sub&gt; cubic P&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;5&lt;/sub&gt; (ZrO)·P&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;7&lt;/sub&gt;</td>
<td>3CaO·P&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;5&lt;/sub&gt; unknown phase SiO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>Y BaO·ZrO&lt;sub&gt;2&lt;/sub&gt;·P&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;5&lt;/sub&gt; unknown phase</td>
</tr>
<tr>
<td>V&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;5&lt;/sub&gt;</td>
<td>ZrO&lt;sub&gt;2&lt;/sub&gt; mon V&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;5&lt;/sub&gt; unknown phase</td>
<td>Sample lost</td>
<td>Y 3BaO·V&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;5&lt;/sub&gt; ZrO&lt;sub&gt;2&lt;/sub&gt; (mon) unknown phase</td>
</tr>
</tbody>
</table>

1See reference 7.
2According to reference 11 a reaction should occur to form 2BaO·ZrO<sub>2</sub>.
3Reference 7 indicates that BaSO<sub>4</sub> reacted easily at 1400°C. Therefore, it is reasonable to assume that some reaction would also take place at 1300°C.
4See reference 7.
5According to reference 11 a reaction should occur to form CaO·SiO<sub>2</sub>.
6According to reference 7, reaction occurred at 1400°C. It is reasonable to assume that reaction would take place at 1300°C also.
7Reaction occurred at 1100°C. It suggests that during the heat up period, Cr<sub>2</sub>O<sub>3</sub> reacted to form uvarovite (3CaO·Cr<sub>2</sub>O<sub>3</sub>·SiO<sub>2</sub>) which later decomposed at a higher temperature.
8According to reference 11, a reaction should occur to form CaO·SiO<sub>2</sub>.
9Reaction occurred at 1100°C. It is reasonable to assume that reaction take place also at 1300°C.
**Title and Subtitle**
REACTION OF CALCIUM ORTHOSILICATE AND BARIUM ZIRCONATE WITH OXIDES AND SULFATES OF VARIOUS ELEMENTS

**Abstract**
Calcium orthosilicate and barium zirconate are being evaluated as the insulation layer of thermal barrier coatings for air-cooled gas turbine components. Their reactions with various oxides and sulfates were studied at 1100° and 1300° C for times to 400 and 200 hours, respectively. These oxides and sulfates represent potential impurities or additives in gas turbine fuels and in turbine combustion air as well as elements of potential bond coat alloys. The phase compositions of the reaction products were determined by X-ray diffraction analysis. $BaZrO_3$ and $2CaO \cdot SiO_2$ both reacted with $P_2O_5$, $V_2O_5$, $Cr_2O_3$, $Al_2O_3$, and $SiO_2$. In addition, $2CaO \cdot SiO_2$ reacted with $Na_2O$, $BaO$, $MgO$, and $CoO$ and $BaZrO_3$ reacted with $Fe_2O_3$.

**Key Words (Suggested by Author(s))**
- Thermal barriers
- Ceramics
- Reactions of oxides

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