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REACTIONS 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 $CaO \cdot SiO_2$) and barium zirconate.

Compounds that reacted with 2 $CaO \cdot SiO_2$: Na_2O, BaO, MgO, CoO, Al_2O_3, Cr_2O_3, SiO_2*, P_2O_5 and V_2O_5.

Compounds that did not react with $2CaO \cdot SiO_2$: Na_2SO_4, K_2O, K_2SO_4, $BaSO_4$, NiO, ZnO and Fe_2O_3.

Compounds that reacted with $BaZrO_3$: Al_2O_3, Cr_2O_3, Fe_2O_3, SiO_2, P_2O_5 and V_2O_5.

Compounds that did not react with $BaZrO_3$: Na_2O, Na_2SO_4, K_2O, K_2SO_4, MgO, CaO, CoO and ZnO.

When comparing these results with data available for reactions between similar compounds and ZrO_2-8w/oY_2O_3 it can be noted that all three materials reacted with SiO_2, P_2O_5 and V_2O_5. 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 Al_2O_3 and Cr_2O_3 which did not react with ZrO_2-8w/oY_2O_3.

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

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*The reaction of SiO_2 with $2CaO \cdot SiO_2$ 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 ZrO_2-12w/oY_2O_3/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 ZrO_2-8w/oY_2O_3 (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 $CaO \cdot SiO_2$ composition, the XRD pattern taken with Cu K_α radiation revealed that this silicate was primarily a monoclinic form, called larnite or β-Ca_2SiO_4 (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, 60PPM 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 ($BaZrO_3$) was prepared by mixing high purity monoclinic ZrO_2 (particle size 1-5 microns) with reagent grade $BaCO_3$ powder and reacting the mixture for 100 hours at 1300°C in a platinum dish. These conditions were sufficient to complete the synthesis of $BaZrO_3$. The completion of the reaction was verified by XRD. All the diffraction lines were accounted for as belonging to $BaZrO_3$ (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 $2CaO \cdot SiO_2$ and $BaZrO_3$: Na_2O, Na_2SO_4, K_2O, K_2SO_4, CaO, BaO, $BaSO_4$, NiO, CoO, MgO, ZnO, Fe_2O_3, Al_2O_3, Cr_2O_3. SiO_2,

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 $2CaO \cdot SiO_2$ or $BaZrO_3$ with the above listed compounds were prepared by thoroughly mixing, in a mortar, 1 gram of $2CaO \cdot SiO_2$ 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 $2CaO \cdot SiO_2$ and $BaZrO_3$ systems are discussed separately.

$CaO \cdot SiO_2$

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 $2CaO \cdot SiO_2$ is uncharted. At 1100°C sodium oxide reacted with larnite. The extent of reaction increased with time. The detected phases were $2CaO \cdot SiO_2$ and $Na_2O \cdot CaO \cdot SiO_2$. After 100 hours at 1300° C the observed phases were also $2CaO \cdot SiO_2$ and $Na_2O \cdot CaO \cdot SiO_2$. However, after 200 hours a new unknown phase appeared and the amount of $Na_2O \cdot CaO \cdot SiO_2$ decreased substantially. This indicates that $Na_2O \cdot CaO \cdot SiO_2$ was unstable at this temperature.

Na_2SO_4

The original mixture contained two compounds, namely $2CaO \cdot SiO_2$ and Na_2SO_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.

K_2O

The existing equilibrium phase diagram in the K_2O-CaO-SiO_2 system is incomplete and does not cover the area connecting K_2O-$2CaO \cdot SiO_2$. XRD analysis of the sample after 200 hours at 1100° C revealed the presence of $2CaO \cdot SiO_2$ 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 $2CaO \cdot SiO_2$ were much better defined. Similar results were obtained at 1300°C. No $CaO \cdot K_2O \cdot SiO_2$ or KOH were detected. Either the K_2O did not react with $2CaO \cdot SiO_2$ and was lost by evaporation or a glassy phase formed, which could not be detected by XRD.

K_2SO_4

The XRD data obtained indicated that, at 1100° C, K_2SO_4 did not react with $2CaO \cdot SiO_4$. After heat treatment at 1300° C for 100 hours, the detected phases were $2CaO \cdot SiO_2$, K_2SO_4 and an unknown compound. Continued heat treatment reduced the amount of K_2SO_4. Because the intensities of diffractions lines produced by $2CaO \cdot SiO_2$ were not affected by the heat treatments, one can conclude that there was no reaction between K_2SO_4 and $2CaO \cdot SiO_2$. The observed unknown phase was probably some form of K_2SO_4.

BaO

According to the existing equilibrium phase diagram for BaO-CaO-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 $(Ba_{1.55} Ca_{0.45}) \cdot SiO_4$. It is reasonable to assume that this compound represents compounds with the general formula $2(Ca_xBa_{1-x}) \cdot SiO_2$. The few unindexed lines were weak and could not be related to $2BaO \cdot SiO_2$, CaO, etc.

$BaSO_4$

No reaction between $2CaO \cdot SiO_2$ and $BaSO_4$ was observed.

MgO

According to the existing equilibrium diagram for the CaO-MgO-SiO_2 system, MgO should react with $2CaO \cdot SiO_2$ to form certain amounts of $3CaO \cdot MgO \cdot SiO_2$ (merwinite). The phases observed after heat treatment at 1100° C were MgO,

$2CaO \cdot SiO_2$ and an unknown compound, isomorphic with $(2CaO \cdot SiO_2)_{5.6}(3CaO \cdot MgO \cdot 2SiO_2)_{4.4}$ (ref. 10). The heat treatment at 1300° caused disappearance of $2CaO \cdot SiO_2$; the remaining phases being the unknown compound and MgO.

NiO

Nickel oxide did not react with larnite at 1100° nor at 1300° C. This observation is in agreement with the tentative CaO-NiO-SiO_2 equilibrium diagram (ref. 11).

CoO

The ternary CaO-CoO-SiO_2 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 $2CaO \cdot SiO_2$ and CoO. At 1300° C the reaction advanced to the point where the predominant phases were CoO and an unknown compound. The strongest XRD-lines of larnite were only detected as a weak line. Thus, it can be stated that CoO reacted with $2CaO \cdot SiO_2$.

ZnO

An equilibrium diagram for the ZnO-CaO-SiO_2 systems exists (ref. 11). In agreement with the diagram, the experimental data indicated that ZnO did not react with larnite at 1100° nor 1300° C. The samples, heat treated at both temperatures, produced well defined XRD patterns of $2CaO \cdot SiO_2$ and ZnO.

Fe_2O_3

At 1100° C no reaction was detected between larnite and Fe_2O_3 (hematite). After heat treatment at 1300° C, the detected phases were larnite, hematite and an unknown compound. According to the existing equilibrium diagram (ref. 11), no reaction should take place between these two compounds.

Al_2O_3

At 1100° and 1300° C, alumina reacted completely with larnite. No free alumina was observed. The detected phases were $2CaO \cdot Al_2O_3 \cdot SiO_2$ and $2CaO \cdot SiO_2$ which is in agreement with the existing equilibrium phase diagram (ref. 11).

Cr_2O_3

At 1100° C, Cr_2O_3 reacted with larnite to give $3CaO \cdot Cr_2O_3 \cdot 3SiO_2$ (uvarovite). No Cr_2O_3 was detected. However, at 1300°C no uvarovite was detected. Only the original compounds, $2CaO \cdot SiO_2$ and Cr_2O_3 were observed. This is consistent with the equilibrium diagram (ref. 11). If the experiment were performed at 1300° C only, one could draw a logical conclusion that Cr_2O_3 did not react with larnite. However, the data obtained at 1100° C suggest that during the heat-up period to 1300° C, Cr_2O_3 reacted with $2CaO \cdot SiO_2$ to form uvarovite which later decomposed at the higher temperature into the two original compounds.

P_2O_5

According to the existing equilibrium diagram (ref. 11) the reaction products should have been $3CaO \cdot P_2O_5$, $CaO \cdot SiO_2$ and SiO_2 (α-cristobalite). However, after heat treatment at 1100° C, the diffraction lines of one or two unknown compounds were detected. The reaction at 1300° C produced $3CaO \cdot P_2O_5$ (calcium orthophosphate) and an unknown compound with an XRD pattern different from the one observed at 1100° C. It was difficult to establish the presence or absence of α-cristobalite because its diffraction lines were coincident with the lines of the unknown compound or compounds.

V_2O_5

Experiments at 1100° C revealed that V_2O_5 (vanadium pentoxide) reacted with larnite to form an unknown compound. Some unreacted V_2O_5 was also found to be present. No larnite was detected. During experiments at 1300° C, the sample crept out of the platinum container and consequently no analysis was performed. Thus, it is reasonable to assume that V_2O_5 reacted at 1300° C with $2CaO$ SiO_2.

$BaZrO_3$

Na_2O

Apparently there was no reaction between Na_2O and $BaZrO_3$. XRD patterns obtained from the samples heat treated at 1100° and 1300° C revealed strong, well defined lines of $BaZrO_3$ and a few weak lines of an unknown phase. No Na_2O, NaOH or Na_2ZrO_3 were detected. Apparently most of Na_2O was lost by evaporation.

Na_2SO_4

At both temperatures, 1100° and 1300° C, no reaction was observed. The samples gave a very strong $BaZrO_3$ pattern and some weak lines which did not correspond to Na_2SO_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.

K_2O

K_2O did not react with $BaZrO_3$ at 1100° or 1300° C. No K_2O was detected. The XRD pattern of $BaZrO_3$ remained unchanged. It is reasonable to assume that K_2O was lost by evaporation.

K_2SO_4

As with Na_2SO_4, $BaZrO_3$ did not react with K_2SO_4. After heat treatments at 1100° and 1300° C, the observed phases were $BaZrO_3$ and some

K_2SO_4. It is of interest to point out that unlike Na_2SO_4, K_2SO_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 1100° or at 1300° 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_2O_3

Analysis of the diffraction patterns of the samples reacted at 1100° and 1300° C revealed that Fe_2O_3 reacted with $BaZrO_3$. The detected phases were $BaZrO_3$, $BaO\cdot 6Fe_2O_3$ 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 $BaO\cdot 6Fe_2O_3$ as $BaZrO_3$ and ZrO_2 have a light color and are not magnetic.

Al_2O_3

The obtained data indicated that Al_2O_3 readily reacted with $BaZrO_3$ at 1100° and 1300° C to form $BaO\cdot Al_2O_3$. In addition to the above compound, the heat treated sample contained $BaZrO_3$ and monoclinic ZrO_2. No Al_2O_3 was detected. (However, in the presence of compounds containing heavy elements like Ba or Zr, small amounts of Al_2O_3 would not be detected.)

Cr_2O_3

At 1100° and 1300° C, Cr_2O_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_2O_3 were observed.

SiO_2

SiO_2 reacted with $BaZrO_3$ at 1100° and 1300° C. In accordance with the existing $BaO-ZrO_2-SiO_2$ equilibrium phase diagram (ref. 11) the detected phases were $2BaO \cdot 2ZrO_2 \cdot 3SiO_2$ and $BaZrO_3$. It appears that the samples heat treated at 1100° C might also contain a small amount of unreacted silica (α-cristobalite).

P_2O_5

At both temperatures, 1100° and 1300° C, P_2O_5 reacted with $BaZrO_3$ to form $BaO \cdot ZrO_2 \cdot P_2O_5$. No $BaZrO_3$ was detected. There were a few XRD lines, some of them relatively strong, that could not be identified.

V_2O_5

V_2O_5 reacted readily with $BaZrO_3$ at 1100° and 1300° C. Even after only 200 hours at 1100° C, all $BaZrO_3$ and V_2O_5 were consumed. The observed phases were $3BaO \cdot V_2O_5$, monoclinic 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° and 1300° 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° and 1300° C produced similar results. When reactions were observed, they were usually the same at both temperatures. If there was no reaction at 1100°, there was generally none at 1300° 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.

Al_2O_3 and Cr_2O_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 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° 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_2O_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_2O_5 and V_2O_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° and 1300° 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 $2CaO \cdot SiO_2$ are Na_2O, BaO, MgO, CoO, Al_2O_3, Cr_2O_3, P_2O_5 and V_2O_5.

The impurities that did not react with $2CaO \cdot SiO_2$ are Na_2SO_4, K_2O, K_2SO_4, $BaSO_4$, NiO, ZnO and Fe_2O_3.

The impurities that reacted with $BaZrO_3$ are Al_2O_3, Fe_2O_3, Cr_2O_3, SiO_2, P_2O_5 and V_2O_5.

The impurities that did not react with $BaZrO_3$ are Na_2O, Na_2SO_4, K_2O, K_2SO_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_2O_3 (7) it was noted that BaO, SiO_2, P_2O_5 and V_2O_5 react with all three materials after 200 hours at 1300° C and that alkali metal sulfates do not react.

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

Temperature	1100° C				1300° C			
Time	200 hr		400 hr		100 hr		200 hr	
Na_2O	$2CaO\cdot SiO_2$ $Na_2O\cdot CaO\cdot SiO_2$	Y	$2CaO\cdot SiO_2$ $Na_2O\cdot CaO\cdot SiO_2$	Y	$2CaO\cdot SiO_2$ $Na_2O\cdot CaO\cdot SiO_2$	Y	$2CaO\cdot SiO_2$ Unknown phase $Na_2O\cdot CaO\cdot SiO_2$ (trace)	Y
Na_2So_4	$2CaO\cdot SiO_2$ Unknown phase	N	$2CaO\cdot SiO_2$ Unknown phase	N	$2CaO\cdot SiO_2$ Unknown phase	N	$2CaO\cdot SiO_2$ Unknown phase	N
K_2O	$2CaO\cdot SiO_2$	N	$2CaO\cdot SiO_2$	N	$2CaO\cdot SiO_2$	N	$2CaO\cdot SiO_2$	N
K_2SO_4	$2CaO\cdot SiO_2$ K_2SO_4	N	$2CaO\cdot SiO_2$ K_2SO_4	N	$2CaO\cdot SiO_2$ K_2SO_4 Unknown phase	N	$2CaO\cdot SiO_2$ unknown phase K_2SO_4 (trace)	N
BaO	$2(Ca_xBa_{1-x})SiO_4$ CaO?	Y	$2(Ca_xBa_{1-x})SiO_2$ CaO?	Y	$2(Ca_xBa_{1-x})\cdot SiO_2$ CaO?	Y	$2(Ca_xBa_{1-x})\cdot SiO_2$ CaO?	Y
$BaSO_4$	$2CaO\cdot SiO_2$ $BaSO_4$	N	$2CaO\cdot SiO_2$ $BaSO_4$	N	$2CaO\cdot SiO_2$ $BaSO_4$	N	$2CaO\cdot Si_2$ $BaSO_4$	N
MgO	MgO $2CaO\cdot SiO_2$	Y	MgO $2CaO\cdot SiO_2$	Y	MgO Unknown phase	Y	MgO Unknown phase	Y
NiO	$2CaO\cdot SiO_2$ NiO	N	$2CaO\cdot SiO_2$ NiO	N	$2CaO\cdot SiO_2$ NiO	N	$2CaO\cdot SiO_2$ NiO	N
CoO	CoO $2CaO\cdot SiO_2$ Unknown phase (trace)	Y	CoO $2CaO\cdot SiO_2$ Unknown phase (trace)	Y	CoO Unknown phase $2CaO\cdot SiO_2$ (trace)	Y	CoO Unknown phase $2CaO\cdot SiO_2$ (trace)	Y
ZnO	$2CaO\cdot SiO_2$ ZnO	N	$2CaO\cdot SiO_2$ ZnO	N	$2CaO\cdot SiO_2$ ZnO	N	$2CaO\cdot SiO_2$ ZnO	N
Fe_2O_3	$2CaO\cdot SiO_2$ Fe_2O_3	N	$2CaO\cdot SiO_2$ Fe_2O_3	N	$2CaO\cdot SiO_2$ Fe_2O_3 Unknown phase	N	$2CaO\cdot SiO_2$ Fe_2O_3 Unknown phase	N
Al_2O_3	$2CaO\cdot Al_2O_3\cdot SiO_2$ $2CaO\cdot SiO_2$	Y	$2CaO\cdot Al_2O_3\cdot SiO_2$ $2CaO\cdot SiO_2$	Y	$2CaO\cdot Al_2O_3\cdot SiO_2$ $2CaO\cdot SiO_2$	Y	$2CaO\cdot Al_2O_3\cdot SiO_2$ $2CaO\cdot SiO_2$	Y
Cr_2O_3	$3CaO\cdot Cr_2O_3\cdot SiO_2$ $2CaO\cdot SiO_2$	Y	$3CaO\cdot Cr_2O_3\cdot SiO_2$ $2CaO\cdot SiO_2$	Y	$2CaO\cdot SiO_2$ Cr_2O_3	Y	$2CaO\cdot SiO_2$ Cr_2O_3	Y
P_2O_5	One or two unknown phases	Y	One or two unknown phases	Y	$3CaO\cdot P_2O_5$ unknown phase SiO?	Y	$3CaO\cdot P_2O_5$ unknown phase SiO?	Y
V_2O_5	Unknown phase some V_2O_5	Y	Unknown phase trace of V_2O_5	Y	Sample lost	Y	Sample lost	Y

TABLE 2. - SUMMARY OF REACTIONS BETWEEN BARIUM ZIRCONATE AND OXIDES AND SULFATE OF VARIOUS ELEMENTS (Y - REACTION WAS DETECTED; N - NO REACTION WAS OBSERVED)

Temperature	1100° C				1300° C			
Time	200 hr		400 hr		100 hr		200 hr	
Na_2O	$BaZrO_3$ unknown phase	N	$BaZrO_3$ unknown phase	N	$BaZrO_3$ unknown phase	N	$BaZrO_3$ unknown phase	N
Na_2SO_4	$BaZrO_3$ unknown phase	N	$BaZrO_3$ unknown phase	N	$BaZrO_3$ unknown phase	N	$BaZrO_3$ unknown phase	N
K_2O	$BaZrO_3$	N	$BaZrO_3$	N	$BaZrO_3$	N	$BaZrO_3$	N
K_2SO_4	$BaZrO_3$ K_2SO_4 (trace)	N	$BaZrO_3$ K_2SO_4 (trace)	N	$BaZrO_3$ K_2SO_4 (trace)	N	$BaZrO_3$ K_2SO_4 (trace)	N
MgO	$BaZrO_3$ MgO	N	$BaZrO_3$ MgO	N	$BaZrO_3$ MgO	N	$BaZrO_3$ MgO	N
CaO	$BaZrO_3$ CaO	N	$BaZrO_3$ CaO	N	$BaZrO_3$ CaO	N	$BaZrO_3$ CaO	N
NiO	$BaZrO_3$ NiO	N	$BaZrO_3$ NiO	N	$BaZrO_3$ NiO	N	$BaZrO_3$ NiO	N
CoO	$BaZrO_3$ CoO	N	$BaZrO_3$ CoO	N	$BaZrO_3$ CoO	N	$BaZrO_3$ CoO	N
ZnO	$BaZrO_3$ ZnO	N	$BaZrO_3$ ZnO	N	$BaZrO_3$ ZnO	N	$BaZrO_3$ ZnO	N
Fe_2O_3	$BaZrO_3$ $BaO \cdot 6Fe_2O_3$ ZrO_2 (mon)	Y	$BaZrO_3$ $BaO \cdot 6Fe_2O_3$ ZrO_2 (mon)	Y Y	$BaZrO_3$ $BaO \cdot 6Fe_2O_3$ ZrO_2 (mon)	Y Y	$BaZrO_3$ $BaO \cdot 6Fe_2O_3$ ZrO_2 (mon)	Y Y
Al_2O_3	$BaZrO_3$ $BaO \cdot Al_2O_3$ ZrO_2 (mon)	Y	$BaZrO_3$ $BaO \cdot Al_2O_3$ ZrO_2 (mon)	Y	$BaZrO_3$ $BaO \cdot Al_2O_3$ ZrO_2 (mon)	Y	$BaZrO_3$ $BaO \cdot Al_2O_3$ ZrO_2 (mon)	Y
Cr_2O_3	$BaCrO_4$ ZrO_2 (mon) Cr_2O_3?	Y	$BaCrO_4$ ZrO_2 (mon) Cr_2O_3?	Y	$BaCrO_4$ ZrO_2 (mon) Cr_2O_3?	Y	$BaCrO_4$ ZrO_2 (mon) Cr_2O_3?	Y
SiO	$2BaO \cdot 2ZrO_2 \cdot 3SiO_2$ $BaZrO_3$ SiO_2 (trace)?	Y	$2BaO \cdot 2ZrO_2 \cdot 3SiO_2$ $BaZrO_3$ SiO_2 (trace)?	Y	$2BaO \cdot 2ZrO_2 \cdot 3SiO_2$ $BaZrO_3$	Y	$2BaO \cdot 2ZrO_2 \cdot 3SiO_2$ $BaZrO_3$	Y
P_2O_5	$BaO \cdot ZrO_2 \cdot P_2O_5$ unknown phase	Y	$BaO \cdot ZrO_2 \cdot P_2O_5$ unknown phase	Y	$BaO \cdot ZrO_2 \cdot P_2O_5$ unknown phase	Y	$BaO \cdot ZrO_2 \cdot P_2O_5$ unknown phase	Y
V_2O_5	$3BaO \cdot V_2O_5$ ZrO_2 (mon) unknown phase	Y	$3BaO \cdot V_2O_5$ ZrO_2 (mon) unknown phase	Y	$3BaO \cdot V_2O_5$ ZrO_2 (mon) unknown phase	Y	$3BaO \cdot V_2O_5$ ZrO_2 (mon) unknown phase	Y

TABLE 3. - COMPARISON OF CHEMICAL REACTIONS BETWEEN ZrO_2 8w/o Y_2O_3, $2CaO\cdot SiO_2$, $BaZrO_3$ AND OXIDES AND SULFATES OF VARIOUS ELEMENTS AFTER 200 hr AT 1300° C
(Y - REACTION WAS DETECTED, N - NO REACTION WAS OBSERVED)

	ZrO_2-8w/o Y_2O_3		$2CaO\cdot SiO_2$		$BaZrO_3$	
Na_2O	ZrO_2 cubic Na_2ZrO_3	Y	$2CaO\cdot SiO_2$ unknown phase $Na_2O\cdot CaO\cdot SiO_2$ (trace)	Y	$BaZrO_3$ unknown phase	N
Na_2SO_4	ZrO_2 cubic ZrO_2 monoclinic unknown phase	N	$2CaO\cdot SiO_2$ unknown phase	N	$BaZrO_3$ unknown phase	N
K_2O	ZrO_2 cubic[1] ZrO_2 monoclinic	Y	$2CaO\cdot SiO_2$	N	$BaZrO_3$	N
K_2SO_4	ZrO_2 cubic ZrO_2 monoclinic unknown phase	N	$2CaO\cdot SiO_2$ unknown phase K_2SO_4 (trace)	N	$BaZrO_3$ K_2SO_4 (trace)	N
BaO	$BaZrO_3$	Y	$2(Ca_xBa_{1-x})\ SiO_2$ CaO	Y	Not tested[2]	Y
$BaSO_4$	Not tested[3]	Y	$2CaO\cdot SiO_2$ $BaSO_4$	N	Not tested	N
MgO	ZrO_2 cubic[4] ZrO_2 mon MgO	N	MgO unknown phase	Y	$BaZrO_3$ MgO	N
CaO	$CaZrO_3$	Y	Not tested[5]	Y	$BaZrO_3$ CaO	N
NiO	ZrO_2 cubic ZrO_2 mon NiO	N	$2CaO\ SiO_2$ NiO	N	$BaZrO_3$ NiO	N
CoO	Not tested[6]	Y	CoO unknown phase $2CaO\cdot SiO_2$ (trace)	Y	$BaZrO_3$ CoO	N
ZnO	ZrO_2 cubic unknown phase	Y	$2CaO\cdot SiO_2$ ZnO	N	$BaZrO_3$ ZnO	N
Fe_2O_3	ZrO_2 cubic ZrO_2 mon Fe_2O_3	N	$2CaO\ SiO_2$ Fe_2O_3 unknown phase	N	$BaZrO_3$ $BaO\cdot 6Fe_2O_3$ ZrO_2 (mon)	Y
Al_2O_3	ZrO_2 cubic ZrO_2 mon Al_2O_3	N	$2CaO\cdot Al_2O_3\cdot SiO_2$ $2CaO\ SiO_2$	Y	$BaZrO_3$ $BaO\cdot Al_2O_3$ ZrO mon	Y
Cr_2O_3	ZrO_2 cubic ZrO_2 mon Cr_2O_3	N	$2CaO\cdot SiO_2$[7] Cr_2O_3	Y	$BaCrO_4$ ZrO_2 mon Cr_2O_2	Y
SiO_2	ZrO_2 cubic ZrO_2 mon SiO_2 $ZrSiO_4$	Y	Not tested[8]	Y	$2BaO\cdot 2ZrO_2 3SiO_2$ $BaZrO_3$	
P_2O_5	ZrO_2 mon ZrO_2 cubic ZrP_2O_3 $(ZrO)_2P_2O_7$	Y	$3CaO\ P_2O_5$ unknown phase SiO_2	Y	$BaO\cdot ZrO_2\ P_2O_5$ unknown phase	Y
V_2O_5	ZrO_2 mon V_2O_5 unknown phase	Y	Sample lost[9]	Y	$3BaO\cdot V_2O_5$ ZrO_2 (mon) unknown phase	

[1] See reference 7.

[2] According to reference 11 a reaction should occur to form $2BaO\cdot ZrO_2$.

[3] Reference 7 indicates that $BaSO_4$ reacted easily at 1400° C. Therefore, it is reasonable to assume that some reaction would also take place at 1300° C.

[4] See reference 7.

[5] According to reference 11 a reaction should occur to form $CaO\ SiO_2$.

[6] According to reference 7, reaction occurred at 1400° C. It is reasonable to assume that reaction would take place at 1300° C, also.

[7] Reaction occurred at 1100° C. It suggests that during the heat up period, Cr_2O_3 reacted to form uvarovite ($3CaO\cdot Cr_2O_3\cdot SiO_2$) which later decomposed at a higher temperature.

[8] According to reference 11, a reaction should occur to form $CaO\cdot SiO_2$.

[9] Reaction occurred at 1100° C. It is reasonable to assume that reaction take place also at 1300° C.

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16 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.

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