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SUMMARY

Zirconia-based coatings are being evaluated as thermal barriers for air-cooled gas-turbine components. The reactions between partially stabilized zirconia, containing 8-weight-percent yttria, and oxides and sulfates of various elements were studied at 1200°, 1300°, and 1400° C for times to 800, 400, and 200 hours, respectively. These oxides and sulfates represent impurities and additives potentially present in gas turbine fuels or impurities in the turbine combustion air as well as the elements of the substrate alloys in contact with zirconia. Based on the results, these compounds can be classified in four groups:

1. Compounds which did not react with zirconia (Na_2SO_4, K_2SO_4, Cr_2O_3, Al_2O_3 and NiO).
2. Compounds that reacted completely with both zirconia phases (CaO, BaO, and BaSO_4).
3. Compounds that reacted preferentially with monoclinic zirconia (Na_2O, K_2O, CoO, Fe_2O_3, MgO, SiO_2, and ZnO).
4. Compounds that reacted preferentially with cubic zirconia (V_2O_5, P_2O_5).

INTRODUCTION

Many attempts have been made to use refractory oxide coatings as thermal barriers between hot combustion gases and cooled rocket and gas turbine engine parts. The desired role of such coatings was to reduce metal temperature and coolant flow requirements or to increase allowable gas temperatures (refs. 1 to 5). For airfoils, little success had been achieved at temperatures above 1100° C. Recently the two-layer thermal barrier coating developed at NASA's Lewis Research Center (refs. 6 and 7) showed significant improvement over earlier efforts. In the cited NASA work a bond coat (~0.005 to 0.010 cm thick) of Ni-16 Cr - 6 Al - 0.6 Y (weight-percent) was plasma sprayed on superalloy substrates and a thermal barrier coating of ZrO_2 - 12 Y_2O_3 (weight-percent) was similarly applied (~0.025 to 0.064 cm thick).
Because thermal barrier coatings are sought which can protect aircraft or utility gas turbine components at very high temperatures, attractive candidates must withstand thousands of heating-cooling cycles and have a long life without reacting with the impurities contained in the combustion gases or with oxides of the elements in the bond coat and the substrate. The purpose of this investigation was to determine the chemical stability of yttria-stabilized zirconia thermal barrier materials in the presence of such chemical compounds. The reactions were studied at 1200°, 1300°, and 1400° C for times to 800, 400, and 200 hours, respectively. However, instead of zirconia containing 12 weight-percent yttria, a zirconia with 8 weight-percent yttria content was used throughout this investigation. The reason for this change was unpublished data obtained by S. Stecura of the Lewis Research Center, which revealed that zirconia containing only 8 weight-percent yttria made a longer lived thermal barrier coating.

EXPERIMENTAL PROCEDURE

Materials

Zirconia used in this investigation was in the form of commercially available plasma spray powder (-200 +325 mesh). It's nominal yttria content was 8 weight-percent. The chemical analysis indicated the presence of the following elements in weight-percent: Al-0.005, Ca-0.055, Si-0.042, Fe-0.035, Ni-0.023, Hf-1.70, Na-<0.001, Li-<0.001, K-<0.001, Mg-0.028, Mo-<0.005, Sr-<0.01, Ti-0.027, W-<0.005, Y₂O₃-7.75, and V-<0.001. XRD analysis of the zirconia powder revealed the presence of both the cubic and monoclinic phases. The cubic phase was the predominant one. No free yttria was detected. Heat treatment of this zirconia powder for 100 hours at 1400° did not produce any changes in the relative amounts of the monoclinic and cubic phases. An examination of the polished zirconia particles under the optical microscope (fig. 1(a)) and of the as-received particles by scanning electron microscope (SEM) techniques (fig. 1(b)) disclosed that the particles had
a sponge-like texture. It appears that each particle was a porous cluster of small grains about 0.0003 cm in diameter.

The following chemical compounds, representing impurities in the fuels and in the combustion air as well as the elements of the substrate alloy were reacted with zirconia: Na$_2$SO$_4$, Na$_2$O, K$_2$SO$_4$, K$_2$O, CaO, BaSO$_4$, BaO, MgO, P$_2$O$_5$, V$_2$O$_5$, Fe$_2$O$_3$, Al$_2$O$_3$, Cr$_2$O$_3$, SiO$_2$, NiO, CoO, and ZnO. For practical reasons instead of Na$_2$O, K$_2$O, CaO, BaO, and CoO, their carbonates were used. Also (NH$_4$)$_2$HPO$_4$ was substituted for P$_2$O$_5$ to facilitate the handling problems. All these compounds were obtained as reagent grade chemicals in powder form. The only exception was SiO$_2$, which was procured in the form of a colloidal suspension.

**Preparation of the Specimens**

Binary mixtures of zirconia and each individual compound were prepared by thoroughly mixing, in a mortar, 1 gram of zirconia with an "equivalent" amount of the compound. The "equivalent" amounts were calculated in the manner that for each atom of Zr there would be an atom of the specific element like Fe, P, Ba, etc. In the case of SiO$_2$ an appropriate amount of colloidal suspension was added to 1 gram of zirconia. The resulting slurry was dried and ground in a mortar.

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 was pinched tightly.

**Heat Treatment and XRD Analysis**

One set of samples so prepared was heated at 1200°C for 400 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 400 hours. Thus we obtained samples which were heat treated for 400 and for 800 hours.
Similarly, the second set of samples was heated at 1300°C for 200 and 400 hours and the third set was heated at 1400°C for 100 and 200 hours.

After each heat treatment, the samples were ground in a mortar and subjected to XRD analysis. In order to qualitatively evaluate the changes in the relative amounts of cubic and monoclinic zirconia, the peak heights of the (111) reflections for both phases were measured and their ratio \( R = \frac{\text{peak height (111) cubic}}{\text{peak height (111) monoclinic}} \) was determined when possible. The \( R \) value, for as-received zirconia, was approximately 6. During analysis of the obtained 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: Phase Diagrams for Ceramists (ref. 8) and Powder Diffraction File Search Manual (ref. 9).

RESULTS

The results obtained in this investigation are shown below. Each system is discussed separately.

\[
\text{Na}_2\text{SO}_4
\]

At 1200°, 1300° and 1400° C Na₂SO₄ did not react with zirconia. Both cubic and monoclinic phases were observed before and after such tests. No known compounds of the ZrO₂-Na₂O or Na₂O-Y₂O₃ systems were detected. Strong lines of some unidentified compound were detected at all temperatures and times. By leaching one of the specimens with water and analyzing the solution and the residue it was found that the solution did not contain zirconium nor yttrium and the residue was composed of cubic and monoclinic zirconia only. It is reasonable to assume that the unknown compound was a form of sodium sulfate. The absence of any reaction between zirconia and sodium sulfate was also observed by S. J. Dapkunas and R. L. Clarke, but at lower temperatures (ref. 5).
In this case sodium carbonate served as a convenient means of introducing Na$_2$O into the system. After heat treatment at all three temperatures the phases obtained were cubic zirconia, Na$_2$ZrO$_3$ and a small amount of an unidentified compound. No monoclinic zirconia was detected. It is reasonable to conclude that Na$_2$O reacted preferentially with monoclinic zirconia to produce Na$_2$ZrO$_3$.

After reacting K$_2$SO$_4$ with stabilized ZrO$_2$ at all three temperatures, the observed phases were: cubic ZrO$_2$, monoclinic ZrO$_2$ and some unknown phase. No K$_2$SO$_4$ or known form of potassium zirconate was detected. The relative amount of monoclinic ZrO$_2$ and of the cubic form containing Y$_2$O$_3$ did not vary significantly indicating that potassium sulfate did not react with zirconia. As in the case of sodium sulfate, by leaching one of the specimens and analyzing the solution and residue it was possible to verify that potassium sulfate indeed did not react with cubic nor monoclinic zirconia. The unknown phase must have been some form of unindexed potassium sulfate.

After exposure at 1200° and 1300° C the observed phases were monoclinic ZrO$_2$ and cubic ZrO$_2$. A few, very weak diffraction lines could not be indexed. No potassium zirconate, K$_2$O, KOH or any Y$_2$O$_3$-K$_2$O compounds were detected. However, the amount of monoclinic ZrO$_2$ relative to cubic ZrO$_2$ increased (R = 2). After 100 hours at 1400° C the observed phases were cubic ZrO$_2$ and K$_2$Zr$_3$O$_7$. However after 200 hours the only phases noted were cubic and monoclinic zirconia. K$_2$Zr$_3$O$_7$ was absent. The behavior of this system could be explained by assuming that K$_2$O initially reacted with monoclinic ZrO$_2$ to form K$_2$Zr$_3$O$_7$, which upon continued heating, decomposed. In the
process K₂O was lost by evaporation. This interpretation of results is compatible with the work of T. Negas et al. on the influence of K₂O on the cerium oxide-ZrO₂ system (ref. 10).

**CaCO₃**

At all three temperatures the reaction product was CaZrO₃ (calcium zirconate). No cubic or monoclinic forms of zirconia were detected.

**BaSO₄**

In the case of BaSO₄ (barium sulfate) the experiment was performed only at 1400°C for 100 and for 200 hours. The observed reaction products were BaZrO₃ (barium zirconate) and some unidentified compound. No free barium sulfate nor monoclinic or cubic zirconias were detected.

**BaCO₃**

This was one of the simplest systems to analyze. At elevated temperatures BaCO₃ decomposed to CO₂ and BaO, which reacted with zirconia to give BaZrO₃. This was the only phase detected after heat treatment at all three temperatures.

**MgO**

At 1200°C MgO (magnesium oxide) reacted very slightly with monoclinic zirconia which could be noted from the small increase in the relative amount of cubic zirconia (R ≈ 6.7). XRD revealed the presence of MgO, cubic ZrO₂ and monoclinic ZrO₂. At 1300°C the relative amount of monoclinic ZrO₂ significantly diminished and it could not be detected at all after heat treatments at 1400°C, in which case only cubic ZrO₂ and MgO were found to be present.
The heat treatments at 1200°, 1300°, and 1400° C produced the following phases: cubic ZrO₂, ZrSiO₄, and SiO₂ (α-cristobalite). Monoclinic zirconia was either not present or it was present only in such small amounts that it was below the XRD detection limits. Another reason for difficulty in detecting monoclinic zirconia was the fact that its diffraction lines coincided with some of those of α-cristobalite and ZrSiO₄. The presence of ZrSiO₄ is the obvious evidence that SiO₂ reacted with zirconia.

Because P₂O₅ would be difficult to handle in the normal ambient environment it was necessary to use (NH₄)₂HPO₄ in order to introduce it into the system. After heat treatment at 1200° and 1300° C the following four phases were detected: cubic ZrO₂, monoclinic ZrO₂, ZrP₂O₇, and (ZrO)₂P₂O₇. The relative amounts of the cubic zirconia as well of ZrP₂O₇ were found to decrease with increasing temperature and time. The values of R after 400 and 800 hours at 1200° C were 1.25 and 0.85, and after 200 and 400 hours at 1300° C they were 0.54 and 0.25, respectively. After heat treatment at 1400° C for 100 and 200 hours only monoclinic ZrO₂ and (ZrO)₂P₂O₇ were detected. These results indicated clearly that P₂O₅ reacted preferentially with cubic ZrO₂ to form ZrP₂O₇ which upon continued heating transformed into (ZrO)₂P₂O₇ (which could be written also as 2ZrO₂·P₂O₅) by losing some P₂O₅. The preferential reaction of P₂O₅ with cubic ZrO₂ was recently reported by H. H. Wilson (ref. 11).

Heat treatments of zirconia-V₂O₅ mixtures at 1200°, 1300°, and 1400° C produced the same type of results. The detected phases were monoclinic ZrO₂, V₂O₅ and some unidentified compound. No cubic ZrO₂
nor known compounds from the $\text{ZrO}_2$-$\text{V}_2\text{O}_5$ or the $\text{Y}_2\text{O}_3$-$\text{V}_2\text{O}_5$ systems were detected. This was a clear indication that $\text{V}_2\text{O}_5$ reacted preferentially with the cubic $\text{ZrO}_2$.

$\text{Fe}_2\text{O}_3$

At all three temperatures $\text{Fe}_2\text{O}_3$ reacted preferentially with monoclinic $\text{ZrO}_2$. After heat treatment at 1400° C no monoclinic $\text{ZrO}_2$ was detected, only cubic $\text{ZrO}_2$ and $\text{Fe}_2\text{O}_3$. At 1200° and 1300° C the amount of monoclinic $\text{ZrO}_2$ decreased with reaction time. Because there was no evidence of the existence of other compounds it is concluded that the result of the reaction between $\text{Fe}_2\text{O}_3$ and monoclinic $\text{ZrO}_2$ was a cubic $\text{ZrO}_2$.

$\text{Cr}_2\text{O}_3$

No reaction was observed between $\text{Cr}_2\text{O}_3$ and zirconia or $\text{Y}_2\text{O}_3$ at any temperature studied.

$\text{Al}_2\text{O}_3$

No reaction was observed between $\text{Al}_2\text{O}_3$ and zirconia or $\text{Y}_2\text{O}_3$ at any temperature studied.

$\text{NiO}$

No reaction was observed between $\text{NiO}$ and zirconia or $\text{Y}_2\text{O}_3$ at any temperature studied.

$\text{CoCO}_3$

At 1400° C $\text{CoCO}_3$ decomposed to $\text{CO}_2$ and $\text{CoO}$, which in turn reacted with monoclinic $\text{ZrO}_2$ to form cubic $\text{ZrO}_2$. The only phases de-
tected by XRD were cubic $\text{ZrO}_2$ and CoO. No experiments were run at 1200° or 1300° C.

**ZnO**

At 1200° and 1300° C ZnO reacted preferentially with monoclinic $\text{ZrO}_2$. The observed phases were cubic $\text{ZrO}_2$, monoclinic $\text{ZrO}_2$ and some unidentified compound. No ZnO was detected. After heat treatment at 1400° C all monoclinic zirconia was gone and so was ZnO. Only cubic $\text{ZrO}_2$ and the unknown compound were detected. It is reasonable to assume that this compound was a result of reaction between monoclinic $\text{ZrO}_2$ and ZnO.

The above described results are summarized in table I. This table lists all the chemical compounds used in this investigation and products of their reactions with zirconia at 1200°, 1300°, and 1400° C. It also includes a column marked with letters N or Y indicating that no reaction took place or that yes, there was a partial or complete reaction.

**DISCUSSION**

Based on the obtained results, the chemical compounds which were used to react with zirconia can be divided into four distinct groups:

Group 1. Chemical compounds that did not react with zirconia: $\text{Na}_2\text{SO}_4$, $\text{K}_2\text{SO}_4$, $\text{Cr}_2\text{O}_3$, $\text{Al}_2\text{O}_3$, and $\text{NiO}$

Group 2. Chemical compounds that reacted completely with zirconia: $\text{CaCO}_3$ (CaO), $\text{BaCO}_3$ (BaO), and $\text{BaSO}_4$

Group 3. Chemical compounds that reacted preferentially with monoclinic $\text{ZrO}_2$: $\text{Na}_2\text{CO}_3$ ($\text{Na}_2\text{O}$), $\text{K}_2\text{CO}_3$ ($\text{K}_2\text{O}$), $\text{CoCO}_3$ (CoO), $\text{Fe}_2\text{O}_3$, MgO, SiO$_2$, and ZnO

Group 4. Chemical compounds that reacted preferentially with cubic $\text{ZrO}_2$: $\text{V}_2\text{O}_5$, $(\text{NH}_4)_2\text{HPO}_4$ ($\text{P}_2\text{O}_5$)
Although in practical use zirconia thermal barriers will operate in an environment much more complex than the conditions under which these experiments were performed, the information obtained from this investigation should prove to be valuable not only in the analysis of the problems one could encounter during testing or use of zirconia thermal barriers in such environments but this information could also be useful in developing new improved barriers. For example, it might not be advisable to use CoCrAlY or FeCrAlY type alloys as the bond coat material because of the reactivity between CoO and Fe₂O₃ and monoclinic zirconia. Also, the use of zirconia thermal barriers in an environment containing particles of iron oxide (near steel mills and foundries) would not be indicated for the same reason. Also, fuel additives containing barium should be avoided because both monoclinic and cubic zirconia react readily with BaO and BaSO₄ to form barium zirconate. It is very significant that neither Na₂SO₄ nor K₂SO₄ reacted with monoclinic and cubic zirconia. These are a few simple examples of the applicability of the information obtained in this investigation.

REFERENCES


### TABLE 1. SUMMARY OF REACTIONS BETWEEN YTTRIA STABILIZED ZIRCONIA WITH OXIDES AND SULFATES OF VARIOUS ELEMENTS

<table>
<thead>
<tr>
<th>Temperature</th>
<th>1200°C</th>
<th>1300°C</th>
<th>1400°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time</td>
<td>400 hr</td>
<td>600 hr</td>
<td>200 hr</td>
</tr>
<tr>
<td>Na₂SO₄</td>
<td>ZrO₂ cubic</td>
<td>ZrO₂ monoclinic</td>
<td>Unknown phase</td>
</tr>
<tr>
<td>Na₂CO₃</td>
<td>ZrO₂ cubic</td>
<td>ZrO₂ monoclinic</td>
<td>Unknown phase</td>
</tr>
<tr>
<td>Na₂ZrO₃</td>
<td>ZrO₂ cubic</td>
<td>ZrO₂ monoclinic</td>
<td>Unknown phase</td>
</tr>
<tr>
<td>K₂SO₄</td>
<td>ZrO₂ cubic</td>
<td>ZrO₂ monoclinic</td>
<td>Unknown phase</td>
</tr>
<tr>
<td>K₂CO₃</td>
<td>ZrO₂ cubic</td>
<td>ZrO₂ monoclinic</td>
<td>Unknown phase</td>
</tr>
<tr>
<td>BaSO₄</td>
<td>Not tested</td>
<td>Not tested</td>
<td>Not tested</td>
</tr>
<tr>
<td>BaCO₃</td>
<td>BaZrO₃</td>
<td>Y</td>
<td>BaZrO₃</td>
</tr>
<tr>
<td>CaCO₃</td>
<td>CaZrO₃</td>
<td>Y</td>
<td>CaZrO₃</td>
</tr>
<tr>
<td>MgO</td>
<td>ZrO₂ cubic</td>
<td>ZrO₂ monoclinic</td>
<td>MgO</td>
</tr>
<tr>
<td>SiO₂</td>
<td>ZrO₂ cubic</td>
<td>ZrO₂ monoclinic</td>
<td>SiO₂</td>
</tr>
<tr>
<td>(NH₄)₂HPO₄</td>
<td>ZrO₂ cubic</td>
<td>ZrO₂ monoclinic</td>
<td>(NH₄)₂HPO₄</td>
</tr>
<tr>
<td>V₂O₅</td>
<td>ZrO₂ monoclinic</td>
<td>V₂O₅</td>
<td>Unknown phase</td>
</tr>
<tr>
<td>Fe₂O₃</td>
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<td>Trace of monoclinic ZrO₂</td>
</tr>
<tr>
<td>Cr₂O₃</td>
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<td>Cr₂O₃</td>
</tr>
<tr>
<td>Al₂O₃</td>
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<td>ZrO₂ monoclinic</td>
<td>Al₂O₃</td>
</tr>
<tr>
<td>N₂O</td>
<td>ZrO₂ cubic</td>
<td>ZrO₂ monoclinic</td>
<td>N₂O</td>
</tr>
<tr>
<td>CoCO₃</td>
<td>Not tested</td>
<td>Not tested</td>
<td>Not tested</td>
</tr>
<tr>
<td>ZrO</td>
<td>ZrO₂ cubic</td>
<td>Unknown phase</td>
<td>Y</td>
</tr>
</tbody>
</table>

*ZrO₂ was reacted with the oxides indicated in the parentheses. Carbonates were the convenient form for handling these oxides.

**P₂O₅** was introduced in the form of (NH₄)₂HPO₄.

* Indicates that no reaction occurred.

0Y indicates a partial or complete reaction.

*a-cristobalite.*
Figure 1. - Microstructure of zirconia spray powder containing 8 wt % Yttria.

(a) As polished cross section. No etch, X250.

(b) SEM, X3000.
Zirconia coatings are being evaluated as thermal barriers for air-cooled gas-turbine components. The reactions of $\text{Y}_2\text{O}_3$ - stabilized zirconia with various oxides and sulfates were studied at $1200^\circ$, $1300^\circ$, and $1400^\circ$ C for times to 800, 400, and 200 hours, respectively. These compounds represent potential impurities or additives in gas turbine fuels and in turbine combustion air as well as elements of the substrate alloys in contact with the zirconia. The phase compositions of the reaction products were determined by x-ray diffraction analysis.