THERMOGRAVIMETRIC STUDY OF THE 800°C REACTION OF ZIRCONIA STABILIZING OXIDES WITH SO₃-NaVO₃

R. L. Jones
Chemistry Division
Naval Research Laboratory
Washington, DC 20375-5000

A thermogravimetric study was made of the reaction of the zirconia stabilizing oxides, In₂O₃, Sc₂O₃, Y₂O₃ and MgO, with molten NaVO₃ at 800°C under SO₃ partial pressures of 10⁻³ to 10⁻⁸ bar. The melt composition is determined by: 2 NaVO₃ + SO₃ ⇌ V₂O₅ + Na₂SO₄. No reaction of In₂O₃ was found at SO₃ partial pressures up to 5 x 10⁻⁴ bar where the reaction, In₂O₃ + V₂O₅ = 2 InV₂O₄, commenced. Reaction of Sc₂O₃ occurred at about 5 x 10⁻⁶ bar of SO₃, with Sc₂O₄ formed. Reaction of Y₂O₃ and MgO with the NaVO₃ melt began, on the other hand, at SO₃ partial pressures too low to be measured (< 10⁻⁷ bar). In₂O₃ and Sc₂O₃ are thus potentially superior to Y₂O₃ and MgO as stabilizers for hot corrosion resistant zirconia thermal barrier coatings. Certain other information concerning the thermochemistry of the SO₂-NaVO₃ system was also revealed.

INTRODUCTION

Stabilized zirconia thermal barrier coatings (TBCs) improve fuel economy and component durability in engines, and are widely used in aero gas turbines (1). TBCs are also beginning to be used in industrial diesel and gas turbine engines. Success in these latter applications has been limited, however, in large part because the stabilizers now commonly used for engine zirconia coatings (Y₂O₃ or MgO) react with the molten vanadate-sulfate deposits formed in engines from the sodium, sulfur and vanadium impurities found in industrial (non-aviation) fuels.

The corrosive vanadate-sulfate deposits are composed of the components, Na₂O, V₂O₅ and SO₃, which are related by reactions [1], [2] and [3]:

\[
\begin{align*}
\text{Na}_2\text{O} (l) + \text{SO}_3 (g) & \rightleftharpoons \text{Na}_2\text{SO}_4 (l) \quad [1] \\
\text{Na}_2\text{O} (l) + \text{V}_2\text{O}_5 (l) & \rightleftharpoons 2 \text{NaVO}_3 (l) \quad [2] \\
2 \text{NaVO}_3 (l) + \text{SO}_3 (g) & \rightleftharpoons \text{Na}_2\text{SO}_4 (l) + \text{V}_2\text{O}_3 (l) \quad [3]
\end{align*}
\]

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Several research groups have shown that the most critical reaction in the vanadate-sulfate hot corrosion of yttria-stabilized zirconia (YSZ) is:

\[ \text{Y}_2\text{O}_3 \text{ (ss)} + \text{V}_2\text{O}_5 \text{ (ls)} \rightleftharpoons 2 \text{YVO}_4 \text{ (s)} \]  \[\text{[4]}\]

In reaction [4], the Y\(_2\)O\(_3\) is in solid solution (ss) in the ZrO\(_2\) matrix, while the V\(_2\)O\(_5\) is in liquid solution (ls) in the deposit melt, and both may thus have activities of well below 1. The YVO\(_4\) product, which occurs as a minimally soluble precipitate, is highly stable (mp 1810°C) and acts as a low activity sink which leaches the Y\(_2\)O\(_3\) stabilizer from the ZrO\(_2\) ceramic.

Reactions of a similar type occur for magnesia-stabilized zirconia (MSZ) where, depending upon the MgO-to-V\(_2\)O\(_5\) ratio, one may have reactions [5], [6] or [7]:

\[
\begin{align*}
\text{MgO (ss)} + \text{V}_2\text{O}_5 \text{ (ls)} & \rightleftharpoons \text{MgV}_2\text{O}_6 & \text{[5]} \\
2 \text{MgO (ss)} + \text{V}_2\text{O}_5 \text{ (ls)} & \rightleftharpoons \text{Mg}_2\text{V}_2\text{O}_7 & \text{[6]} \\
3 \text{MgO (ss)} + \text{V}_2\text{O}_5 \text{ (ls)} & \rightleftharpoons \text{Mg}_3\text{V}_2\text{O}_8 & \text{[7]} \\
\end{align*}
\]

The decomposition temperatures for these compounds are about 640°C for MgV\(_2\)O\(_6\), 740°C for Mg\(_2\)V\(_2\)O\(_7\), and 1100°C for Mg\(_3\)V\(_2\)O\(_8\). Dosages of 3 MgO to 1 V\(_2\)O\(_5\), which produce Mg\(_3\)V\(_2\)O\(_8\), give best results when magnesium is used to inhibit high temperature corrosion caused by vanadium in the fuel (2).

In addition to reaction with V\(_2\)O\(_5\), Y\(_2\)O\(_3\) (3,4) and MgO may also react with SO\(_3\) in the presence of Na\(_2\)SO\(_4\) to produce low melting mixed sulfates as indicated in reactions [8] and [9]:

\[
\begin{align*}
\text{Y}_2\text{O}_3 \text{ (ss)} + 3 \text{SO}_3 \text{ (g)} \left( + \text{Na}_2\text{SO}_4 \right) & \rightleftharpoons \text{Y}_2\text{(SO}_4)_3\text{-Na}_2\text{SO}_4 \text{ (l)} & \text{[8]} \\
\text{MgO (ss)} + \text{SO}_3 \text{ (g)} \left( + \text{Na}_2\text{SO}_4 \right) & \rightleftharpoons \text{MgSO}_4\text{-Na}_2\text{SO}_4 \text{ (l)} & \text{[9]} \\
\end{align*}
\]

Reaction [8] goes readily at 800°C under SO\(_3\) partial pressures as low as 5 x 10\(^4\) bar (4). The sulfation of MgO by reaction [9] is also highly favored, with SO\(_3\) and V\(_2\)O\(_5\) being known to compete for reaction with MgO when magnesium inhibitors are used with low quality fuel (2,5).

Our earlier research indicated that reaction between the TBC ceramic oxides and the corrosive molten deposit oxides is largely controlled by a Lewis acid-base reaction mechanism (6). Working from this basis, we have since identified scandia (7) and india (8) as potential corrosion-resistant stabilizers for zirconia TBCs.

We report here a thermogravimetric study intended to help understand and quantify the reactions between the different zirconia stabilizing oxides and vanadate-sulfate molten deposits. In this study, we consider NaVO\(_3\) to simulate an engine deposit.
having a Na/V ratio of 1) that exists in equilibrium with the SO₃ in the combustion gas. The equilibrium is described by reaction [3] above. Thermodynamic calculations by Luthra and Spacil (9) indicate that reaction [3] should be the predominant reaction under gas turbine conditions.

In our experimental approach, we study reaction [3] by equilibrating NaVO₃ with increasing partial pressures of SO₃ in the thermobalance and determining, from weight gain, the concentrations of V₂O₅, Na₂SO₄ and NaVO₃ produced at each SO₃ pressure. Repeating the NaVO₃ equilibrium experiments, but with the various stabilizing oxides added, then serves to pinpoint the SO₃ partial pressures at which the melt V₂O₅ activity is raised sufficiently by reaction [3] that reaction (i.e., reaction [4]) between the stabilizing oxide and the melt V₂O₅ commences. This procedure provides a ranking of the reaction resistance of the stabilizing oxides, as well as certain information on the thermochemistry of their reaction with vanadate/sulfate melts. It has been applied here to study and compare the zirconia stabilizing oxides, Y₂O₃, MgO, Sc₂O₃, and In₂O₃.

EXPERIMENTAL

The required low partial pressures of SO₃ were produced by a two-stage SO₂/air dilution system using Tylan FC-260 mass flow gas controllers having 0-10 scm (for SO₂) and 0-5 slm (for air) flow rate ranges (Fig. 1). After being dried over an indicating anhydrous CaSO₄ drying agent, tank SO₂ (Matheson, 99.98%) and laboratory air were passed into the first stage of dilution where, by using 0.5 scm of SO₂ and 5 slm of air, dilutions of up to 10⁻⁴ could be achieved. Total dilutions of up to 10⁻⁸ were possible by second stage dilution. The diluted SO₂/air then passed into a manifold, from which samples were withdrawn for analysis by H₂O₂ absorption (10), and finally into a Cahn 1000 thermobalance (Fig. 2). The SO₂/air mixture was equilibrated over a Pt catalyst at temperature, as shown in Fig. 2, with the resultant SO₃ concentration calculated. Controlled (± 10%) SO₃ partial pressures over the range of 10⁻³ to 10⁻⁸ bar, along with a balance sensitivity of 0.1 mg, were provided by the system. Furnace temperatures were maintained within ± 5°C using a three-zone furnace (Applied Test Systems 3210) and electronic temperature controller (Omega CN9121).

The sample sizes were 0.41 millimoles (50mg) for NaVO₃, and 0.10 mmols for the stabilizing oxides, except for MgO which was 0.20 mmols. (Note: the NaVO₃ contained about 2% water, and our practice was to weigh out 51mg of NaVO₃ which reduced to approximately 50mg after H₂O loss on heatup.) The samples were weighed directly into a platinum planchet using a Mettler AE 160 bench balance, and the planchet then transferred to the Cahn 1000 thermobalance. The chemical reagents used were NaVO₃ (Johnson Matthey, 98%), Y₂O₃ (Rare Earth Pdts, 99.9999%), MgO (Johnson Matthey, 99.9998%), Sc₂O₃ (Rare Earth Pdts, 99.99%), and In₂O₃ (Johnson Matthey, 99.99%). At the end of selected experiments, the specimen samples were ground and subjected to x-ray diffraction to help identify the reaction products.
RESULTS AND DISCUSSION

Reversibility and Reproducibility

Preliminary tests established that reaction [3] was reversible and reproducible at 700 and 800°C. These properties are demonstrated for 700°C in Fig. 3a. (NB, the indicated SO₃ values in Figs. 3a and 3b are only relative, and not absolute, since the Pt catalyst was not at proper temperature in these initial trials.) A sample of NaVO₃ (solid line) was equilibrated with 50 Pa of SO₃, and then the SO₃ pressure reduced to 11 Pa, and the NaVO₃ reequilibrated, with corresponding weight loss, at this new pressure. A second NaVO₃ sample (dashed line) was equilibrated with 11 Pa of SO₃ (coming to the same weight as in the first experiment), and the sample then reequilibrated under 5 Pa of SO₃. Finally, a third NaVO₃ sample (short dashed line) was equilibrated under 5 Pa of SO₃, with the same weight gain as in the second experiment. In each case, identical equilibria were reached, regardless of whether approached from higher or lower SO₃ partial pressure.

Detection of Ceramic Oxide Reaction

Fig. 3b compares the weight gain curves obtained for pure NaVO₃ (from Fig. 3a) with the curves produced when mixtures of 0.1 mmol In₂O₃/0.4 mmol NaVO₃ were equilibrated at the same 50, 11, and 5 Pa of SO₃. Note that a pronounced increment of additional weight gain is produced with the In₂O₃-NaVO₃ mixtures at 50 and 11 Pa of SO₃, but not at 5 Pa of SO₃ where the total weight gain is in fact slightly lower with the presence of In₂O₃. This behavior results because the melt V₂O₅ activity is increased enough, via reaction [3], at 50 and 11 Pa of SO₃ to allow V₂O₅ reaction with In₂O₃ to form InV₂O₄ (see below). At 5 Pa of SO₃, the critical V₂O₅ activity required for reaction with In₂O₃ is not reached, and so no weight gain or InV₂O₄ formation is seen.

Kinetics of reaction

Note that the rate of weight gain in Fig. 3b, although different for the various SO₃ pressures, is nearly constant until near equilibrium, and that it is not changed when In₂O₃ is present. This implies that the rate-controlling step is associated with the uptake of SO₃ into the NaVO₃ melt, and not with the subsequent reaction between In₂O₃ and V₂O₅. Division of the weight gain rate by the SO₃ concentration indicates the rate-controlling reaction to be first order with respect to SO₃, although the weight gain rate/SO₃ concentration quotient decreases slightly with concentration, going from 0.0312 at 5 Pa of SO₃ to 0.0260 at 50 Pa of SO₃.
Insuring Equilibrium at Low SO$_3$ Pressures

Since the rate of reaction is inversely proportional to the SO$_3$ partial pressure, progressively longer times are required for equilibrium as the SO$_3$ pressure decreases. This problem was alleviated by driving reaction [3] to near equilibrium under high SO$_3$ pressure, and then reducing to the test SO$_3$ level and determining the closeness to equilibrium from the slope of the ensuing weight gain trace. An example is shown in Fig. 4 for Y$_2$O$_3$-NaVO$_3$ under 0.06 Pa of SO$_3$ at 800°C. A higher SO$_3$ partial pressure (of about 200 Pa) was applied in 5 stages, with the ensuing slope under 0.06 Pa of SO$_3$ being positive up to the fourth stage (at 11.4 mg) where the slope was very slightly positive, and the fifth stage (at 12.1 mg) where the slope was clearly negative. True equilibrium (approached from both below and above) therefore lies at about 11.5 mg weight gain.

Equilibrium of SO$_3$ with Pure NaVO$_3$

Using the technique above for achieving equilibrium, and with the furnace heat zones properly adjusted so that the Pt catalyst was within ± 5°C of the specimen temperature, we determined the equilibrium weight gain for NaVO$_3$ at 700° and 800°C under SO$_3$ partial pressures ranging from approximately $1 \times 10^{-3}$ to $5 \times 10^{-8}$ bar. The results are shown in Fig. 5 in terms of SO$_3$ activity.

Nonideality of Solution Behavior

Using thermodynamic data compiled by Luthra and Spacil (9), one can calculate the Gibbs standard free energy for reaction [3], which is $-49.560$ kJ and $-40.316$ kJ at 700° and 800°C respectively. Then, assuming ideal behavior on the part of all species, and knowing the equilibrium SO$_3$ partial pressures or activities, it is possible to calculate the ideal solution behavior of V$_2$O$_5$ for each SO$_3$ pressure and temperature on the basis of the relationships:

$$\Delta G^o = -RT \ln K$$  \hspace{1cm} [10]

and, where $K$ is the equilibrium constant,

$$K = \frac{(a_{NaSO_3})(a_{V_2O_5})}{(a_{NaVO_3})^2(a_{SO_3})}$$  \hspace{1cm} [11]

In addition, noting that the SO$_3$ concentration is below $10^{-3}$ in the melt and negligible in terms of mole-fraction calculation, one can use the equilibrium weight gain data to determine the experimental V$_2$O$_5$ concentration produced for each set of conditions. This

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allows a comparison between the ideal and experimental solution behavior for $V_2O_3$ at 700° and 800°C, as shown in Fig. 6. Note, however, that while this comparison is useful for showing that $V_2O_3$ deviates significantly from ideal behavior, it provides no information as to the actual $V_2O_3$ activity.

Observations Concerning Association in the Melt

The $SO_3$ addition to $NaVO_3$ can be viewed as being an acid-base "titration" of the polybasic $Na_2O-V_2O_5$ system. This would be analogous to the neutralization of polybasic acids such as $H_3PO_4$ by strong bases, where the titration curve of ml of titrant vs. pH takes a multi-step form as a result of the progressive dissociation of the polybasic acid molecule. However, the weight gain vs. log of $SO_3$ activity curves in Fig. 5 are smoothly monotonic, and show no sign of a step-wise break in slope. This implies, assuming our analogy is correct, that no strong association or dissociation is occurring in the given $V_2O_5-Na_2SO_4-NaVO_3$ system within the $SO_3$ activity range being investigated.

Reaction of $In_2O_3$ with $SO_3-NaVO_3$

The reaction of $In_2O_3$ with $SO_3-NaVO_3$ was investigated by experiments similar to those above, but with 0.10 mmols of $In_2O_3$ added. The 800°C test temperature was chosen because earlier results (8) indicated that there should be little reaction between $SO_3$ and $In_2O_3$ at this temperature for the $SO_3$ levels under study.

The $SO_3-In_2O_3-NaVO_3$ results are plotted in Fig. 7 along with the "baseline" 800°C $SO_3-NaVO_3$ equilibrium curve (from Fig. 5). The $In_2O_3-NaVO_3$ data are essentially parallel (although slightly lower) to the pure $NaVO_3$ weight curve up to an $SO_3$ activity of about $5 \times 10^4$, where the $In_2O_3-NaVO_3$ data show an abrupt increase of approximately 5-6mg above the $NaVO_3$ weight gain curve.

The upward break in the $In_2O_3-NaVO_3$ weight curve marks the point at which the melt $V_2O_3$ activity has been raised high enough, by reaction [3], that $In_2O_3$ begins to react with $V_2O_3$ to form $InVO_4$. This is confirmed by comparison of x-ray patterns from specimens A and B (as marked in Fig. 7) with standard patterns for pure $InVO_4$ (synthesized in our laboratory) and cubic $In_2O_3$ (JCPDS 6-0416). As Fig. 8 shows, the pattern from Spec. A contains the major lines for $InVO_4$, but not those for $In_2O_3$, while the pattern from Spec. B agrees well with that of $In_2O_3$, but not $InVO_4$. India is therefore the stable indium form up to an $SO_3$ activity of about $5 \times 10^4$, with $InVO_4$ being stable thereafter. The relative intensities of the $InVO_4$ peaks for Spec. A are distorted, but this is probably only because the $InVO_4$ forms with a crystal habit that leads to a high degree of orientation in the powder specimen.

The weight gain behavior is also consistent with an oxide-to-metavanadate transition at the $SO_3$ activity of $5 \times 10^4$. The only source of weight gain in our system
is from \( \text{SO}_3 \) uptake into the melt, and the maximum possible weight gain for 50mg of \( \text{NaVO}_3 \) is 16.4mg, which corresponds to complete conversion of the \( \text{NaVO}_3 \) to \( \text{Na}_2\text{SO}_4 \) and \( \text{V}_2\text{O}_5 \) by reaction [3]. On the other hand, total conversion of 0.10 mmols of \( \text{In}_2\text{O}_3 \), \( \text{Y}_2\text{O}_3 \), or \( \text{Sc}_2\text{O}_3 \) to the metavanadate via reaction [4] would consume 0.10 mmols of \( \text{V}_2\text{O}_5 \) from the \( \text{NaVO}_3 \), which would make 0.10 mmols of \( \text{Na}_2\text{O} \) available for reaction with \( \text{SO}_3 \) by reaction [2], and thus lead to a weight gain of 8.2mg. The weight gain step for \( \text{In}_2\text{O}_3-\text{NaVO}_3 \) in Fig. 7 is only 5-6mg, but note that 10mg of weight gain occurs before \( \text{InVO}_4 \) formation begins (a high \( \text{V}_2\text{O}_5 \) activity is required), and that the final combined weight gain of 15-16mg essentially equals the 16.4mg maximum possible weight gain for the specimen.

If the oxide and metavanadate in reaction [4] are pure solids and their standard energies of formation are known, then the \( \text{V}_2\text{O}_5 \) activity required for the commencement of reaction [4] can be calculated. For example, on the basis of thermodynamic data from Hwang and Rapp (11) and Turkdogan (12), the \( \text{V}_2\text{O}_5 \) activity necessary for reaction with \( \text{Y}_2\text{O}_3 \) to form \( \text{YVO}_4 \) at 900°C can be calculated to be about \( 1 \times 10^{-5} \). Mittal and Elliott (13) have determined the activity of \( \text{V}_2\text{O}_5 \) in 50 mole-percent \( \text{Na}_2\text{O}-\text{V}_2\text{O}_5 \) (i.e., \( \text{NaVO}_3 \)) by electrochemical measurement as being \( 5 \times 10^{-4} \) at 850°C. One can predict therefore that \( \text{Y}_2\text{O}_3 \) should react with pure \( \text{NaVO}_3 \) to form \( \text{YVO}_4 \) (as in fact we see below).

Unfortunately the standard energy of formation for \( \text{InVO}_4 \) is not known, and so the \( \text{V}_2\text{O}_5 \) activity for \( \text{InVO}_4 \) formation can not be calculated directly. However, from Fig. 7, we know that the \( \text{V}_2\text{O}_5 \) activity for \( \text{InVO}_4 \) formation is higher than the \( 5 \times 10^{-4} \) \( \text{V}_2\text{O}_5 \) activity of pure \( \text{NaVO}_3 \). If we postulate that interaction of \( \text{SO}_3 \) with the melt increases the \( \text{V}_2\text{O}_5 \) activity to \( 5 \times 10^{-3} \) or \( 5 \times 10^{-2} \) (i.e., by 1 or 2 orders of magnitude), the corresponding free energies for \( \text{InVO}_4 \) formation by reaction [4] would be \(-47.3 \text{kJ} \) or \(-26.7 \text{kJ} \), respectively. These two values would then lead, since the known standard energies of formation for \( \text{V}_2\text{O}_5 \) (1) (9) and \( \text{In}_2\text{O}_3 \) (s) (12) are known, to an estimated energy of formation for \( \text{InVO}_4 \) at 800°C of \(-870 \text{kJ/mole} \) (for \( 5 \times 10^{-3} \) \( \text{V}_2\text{O}_5 \) activity) or \(-860 \text{kJ/mole} \) (for \( 5 \times 10^{-2} \) \( \text{V}_2\text{O}_5 \) activity). Furthermore, since the \( \text{V}_2\text{O}_5 \) mole-fraction in the melt at \( \text{InVO}_4 \) formation is approximately 0.3 (as read from Fig. 6 at the critical \( \text{SO}_3 \) activity of \( 5 \times 10^{-4} \)), we can estimate the activity coefficient for \( \text{V}_2\text{O}_5 \) at this concentration to be of the order of \( 2 \times 10^{-4} \) to \( 2 \times 10^{-1} \).

**Reaction of \( \text{Sc}_2\text{O}_3 \) and \( \text{Y}_2\text{O}_3 \) with \( \text{SO}_3-\text{NaVO}_3 \)**

Similar experiments with \( \text{Sc}_2\text{O}_3 \) and \( \text{Y}_2\text{O}_3 \) produced the results given in Fig. 9. Note that the predicted weight gain step of about 8mg is seen with these more reactive oxides, especially at the lower \( \text{SO}_3 \) activities. The critical \( \text{SO}_3 \) activity for reaction of \( \text{Sc}_2\text{O}_3 \) with the melt \( \text{V}_2\text{O}_5 \) is shown to be about \( 5 \times 10^{-4} \) in Fig. 9. X-ray diffraction confirmed that \( \text{ScVO}_4 \) is the stable scandium phase at \( \text{SO}_3 \) activities higher than \( 5 \times 10^{-6} \).
Some ScVO$_4$ is detected, however, (although the majority scandium phase is Sc$_2$O$_3$) below the critical $5 \times 10^{-6}$ SO$_3$ activity. This is not unexpected since pure NaVO$_3$ may have sufficient V$_2$O$_5$ activity at 800°C to allow ScVO$_4$ formation (14). The production of ScVO$_4$ consumes V$_2$O$_5$ and lowers the V$_2$O$_5$ activity of the NaVO$_3$ melt (especially if the Sc$_2$O$_3$/NaVO$_3$ ratio is high), so that only limited ScVO$_4$ formation occurs. When SO$_3$ is present, at activities above $5 \times 10^{-6}$, it reacts with the Na$_2$O generated in the melt because of V$_2$O$_5$ consumption (cf. reaction [2]), and maintains the melt V$_2$O$_5$ at a level which drives the conversion of Sc$_2$O$_3$ to ScVO$_4$ essentially to completion.

The reaction behavior of Y$_2$O$_3$ with SO$_3$-NaVO$_3$ is similar, except that Y$_2$O$_3$, presumably because it is a more basic oxide than Sc$_2$O$_3$ (14), reacts more readily than Sc$_2$O$_3$ with NaVO$_3$. There is a substantial conversion of Y$_2$O$_3$ to YVO$_4$ by reaction with NaVO$_3$ alone, as shown experimentally (6) and predicted by thermodynamics (see above). It is not possible therefore to identify an SO$_3$ partial pressure that leads to the onset of reaction of Y$_2$O$_3$ with NaVO$_3$. The effect of SO$_3$ in driving full conversion of Y$_2$O$_3$ to YVO$_4$ can be seen in Fig. 9, however, as manifested by the near 8mg weight gain produced even at SO$_3$ activities in the $10^{-7}$ range.

**Reaction of MgO with SO$_3$-NaVO$_3$**

The results for the reaction of MgO with SO$_3$-NaVO$_3$ are given in Fig. 10. The weight gain curve for SO$_3$-MgO-NaVO$_3$ lies above the SO$_3$-NaVO$_3$ equilibrium curve at all SO$_3$ activities, being roughly parallel to the SO$_3$-NaVO$_3$ curve at the lowest SO$_3$ activities, but then diverging upward as the SO$_3$ activity increases. One may speculate that the weight gain at the lower SO$_3$ activities results from MgSO$_4$ formation, with Mg-vanadate formation (perhaps Mg$_3$V$_2$O$_8$ since MgO is initially in excess) then coming into play as the V$_2$O$_5$ activity increases. Some evidence of a break in the MgO weight gain curve may be seen, as suggested by the dashed lines in Fig. 10. However, the x-ray diffraction patterns produced by the MgO-melt specimens are complex, and it has not been possible to verify that Mg-vanadate formation in fact commences in the vicinity of the "break point" indicated in Fig. 10.

**CONCLUSIONS**

The reaction of zirconia stabilizing oxides with molten vanadate-sulfate salts under SO$_3$ equilibrium can be successfully studied by high temperature thermogravimetry, and the resistance of the individual oxides to reaction with the vanadate-sulfate melt quantitatively evaluated.

The results show Sc$_2$O$_3$, and especially In$_2$O$_3$, to be more resistant than Y$_2$O$_3$ and MgO to reaction with 800°C vanadate-sulfate melts. Scandia and indium are thus potentially superior to yttria and magnesia for use as stabilizers to produce zirconia.
thermal barrier coatings having improved resistance to molten vanadate-sulfate hot corrosion.

The method is limited to SO₃ activities of 10⁻⁸ and upward, but this covers the range of SO₃ activities likely to be encountered in technology. For example, the SO₃ partial pressure in an industrial gas turbine (CH₄ fuel, 10/1 compression, 30/1 air-to-fuel, 800°C) is of the order of 5 x 10⁻⁶ for fuel with 0.01% sulfur (aviation fuel allows up to 0.05%) and 5 x 10⁻⁴ for fuel containing 1% sulfur (typical of industrial fuels). The effect of the Na/V ratio in engine deposits, which may well also be critical, can be studied by changing the Na/V ratio in the thermobalance vanadate specimen.

Thermogravimetric study of SO₃ equilibrium with vanadate-sulfate melts has the potential for providing new information on the thermodynamics and solution chemistry of the technologically important molten vanadate-sulfate salt system.

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REFERENCES

1. F. C. Toriz, A. B. Thakker and S. K. Gupta, Surface and Coatings Technol., 39/40, 161 (1989).

2. T. N. Rhys-Jones, J. R. Nicholls and P. Hancock, Corrosion Sci., 23, 139 (1983).

3. R. H. Barkalow and F.S. Pettit, in "Proc. of the 1st Conf. on Advanced Materials for Alternative Fuel Capable Directly Fired Heat Engines," J. W. Fairbanks and J. Stringer, Editors, p. 704, NTIS, Springfield, VA (1979).

4. R. L. Jones, D. B. Nordman and S. T. Gadomski, Metall. Trans. A, 16A, 303 (1985).

5. J. J. Macfarlane, in "The Mechanism of Corrosion by Fuel Impurities," pp. 261-275, Butterworths, London (1963).

6. R. L. Jones, C. E. Williams and S. R. Jones, J. Electrochem. Soc., 133, 227 (1986).
7. R. L. Jones, in "Corrosion and Corrosive Degradation of Ceramics: Ceramics Transactions, Vol. 10," R. E. Tressler and M. McNallan, Editors, p. 291, The American Ceramic Society, Westerville, OH (1990).

8. R. L. Jones and D. Mess, submitted for publication in J. Am. Ceram. Soc.

9. K. L. Luthra and H. S. Spacil, J. Electrochem. Soc., 129, 649 (1982).

10. A. W. Berger, J. N. Driscoll and P. Morgenstern, P. Am. Ind. Hygiene Assoc., 33, 397 (1972).

11. Y.-S. Hwang and R. A. Rapp, Corrosion, 45, 933 (1989).

12. E. T. Turkdogan, "Physical Chemistry of High Temperature Technology," pp. 5-24, Academic Press, New York (1980).

13. S. K. Mittal and J. F. Elliott, J. Electrochem. Soc., 131, 1194 (1984).

14. R. L. Jones, Surface and Coatings Technol., 39/40, 89 (1989).
Fig. 1 Schematic of SO$_2$/air gas dilution system.

Fig. 2 Schematic of thermobalance system.
Fig. 3(a)-3(b) Weight gain behavior showing (3a) reversibility and reproducibility of $\text{SO}_3$-$\text{NaVO}_3$ equilibrium at 700°C, and (3b) reaction of $\text{In}_2\text{O}_3$ at 50 and 11, but not 5, Pa of $\text{SO}_3$.

Fig. 4 Weight gain trace illustrating determination of equilibrium of 0.06 Pa of $\text{SO}_3$ with $\text{Y}_2\text{O}_3$-$\text{NaVO}_3$ at 800°C.

Fig. 5 Equilibrium weight gain for $\text{SO}_3$-$\text{NaVO}_3$ reaction as a function of $\text{SO}_3$ activity at 700 and 800°C.
Fig. 6 Mole-fraction of $V_2O_5$ vs. $SO_3$ activity, as (1) calculated assuming ideal behavior, and (2) determined from weight gain.

Fig. 7 Comparison of weight gain for pure NaVO$_3$ vs. In$_2$O$_3$-NaVO$_3$ at 800°C as a function of $SO_3$ activity.

Fig. 8 X-ray diffraction spectra from Specimens A and B of Fig. 7 confirming transition from In$_2$O$_3$ to InVO$_4$ at $SO_3$ activity of 5 x 10$^{-4}$.
Fig. 9 Weight gain behavior for $\text{Sc}_2\text{O}_3-\text{NaVO}_3$ and $\text{Y}_2\text{O}_3-\text{NaVO}_3$ at 800°C as function of SO$_3$ activity.

Fig. 10 Comparison of weight gain behavior for MgO-\text{NaVO}_3 vs. pure NaVO$_3$ at 800°C as function of SO$_3$ activity.