SOLUBILITY OF CeO₂ IN MOLTEN Na₂SO₄-10 mol% NaVO₃ SALT SOLUTION AT 900°C

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ABSTRACT
The solubility of CeO₂ was measured as a function of melt basicity in a Na₂SO₄-10 mol% NaVO₃ solution at 900°C and 1 atm oxygen. The results indicate that CeO₂ dissolves in the salt solution either as a basic or as an acidic solute. The dissolution reactions were derived from the dependence of the solubility on solvent basicity. A comparison of the CeO₂ solubility in Na₂SO₄-10 mol% NaVO₃ with the solubilities in both pure Na₂SO₄ and in Na₂SO₄-30 mol% NaVO₃ is made. The results agree quantitatively with a theory based on the "common component effect".

KEYWORDS hot corrosion, vanadate, dissolution

INTRODUCTION
Vanadium, sodium and sulfur are common impurities in low-grade fossil fuels. As "clean" fuel resources diminish, these low-grade fuels come into use in engines. The condensation of combustion products of such fuels leads to molten salt deposits containing vanadium, such as NaVO₃ and V₂O₅, in addition to sulfates (1). These deposits are known to be very corrosive to high temperature materials and coatings in combustion systems (2). For example, although Y₂O₃-stabilized ZrO₂ thermal barrier coatings offer a good match in thermal expansion coefficient and generally exhibit chemical stability when in contact with a thin film of fused sulfate deposit, the coatings have been found to destabilize as the Y₂O₃ is leached from the ceramic by a Na₂SO₄-NaVO₃ deposit in an O₂/SO₂/SO₃ gas atmosphere (3,4). The chemical stabilities of various oxides, such as Y₂O₃, CeO₂, HfO₂, In₂O₃, Sc₂O₃ and ZrO₂, in V₂O₅ and vanadate or sulfate fused salt solutions have been studied by Jones et al. (5-9).

As a knowledge of metal oxide solubilities in molten salt solutions is of great importance in evaluating the hot
corrosion resistance of these materials, the solubilities of CeO₂, HfO₂ and Y₂O₃ in Na₂SO₄-30 mol% NaVO₃ solution were measured as a function of solvent basicity at 900°C and 1 atm oxygen (10). For comparison, the solubility of CeO₂ in pure fused Na₂SO₄ was also determined. Assuming an ideal solution for the Na₂SO₄-30 mol% NaVO₃ system, Hwang and Rapp (11) derived the equilibrium distribution of vanadate derivatives, which leads to a theoretical prediction for the dependence of oxide solubilities on salt composition. Following the results of references (10) and (11), in the present study, the solubility of CeO₂ was measured in a Na₂SO₄-10 mol% NaVO₃ salt solution as a function of melt basicity at 900°C and 1 atm oxygen. A comparison of the CeO₂ solubility in Na₂SO₄-10 mol% NaVO₃ with the solubilities in both pure Na₂SO₄ and in Na₂SO₄-30 mol% NaVO₃ is made, and the prediction made by Hwang and Rapp is evaluated.

EXPERIMENTAL PROCEDURES

The chemicals used in this study were 99.9% pure CeO₂ powder, 99% NaVO₃ powder and reagent grade Na₂SO₄. The NaVO₃ was dehydrated at 400°C for 8 hrs. The CeO₂ and Na₂SO₄ were dried at ~110°C in an oven for at least 4 hrs before use. For each experiment, ~1.5 g CeO₂ powder was charged into an alumina crucible with ~20 g of salt mixture of Na₂SO₄-10 mol% NaVO₃. The chemicals were further dried at 400°C overnight before heating the system to 900°C. Na₂O₂ was added, or catalyzed O₂-SO₂ mixed gas with different compositions was introduced to the system to adjust the melt basicity in the range of -13.0 ≤ log aₙa₂o ≤ -7.8.

The electrochemical reference electrodes used previously (10,12) were employed in the present study to monitor the melt basicity and oxygen activity. A sodium sensor consisting of a piece of silver wire contacting a Na₂SO₄-10 mol% Ag₂SO₄ salt solution contained in a fused SiO₂ (GE 214) tube, which is a good Na⁺ conductor at high temperature. The SiO₂ tube was sealed at the top with alumina-base Ceramabond, and a platinum wire spot-welded to the silver wire was used as a lead wire. The other reference electrode, an oxygen probe, was composed of a Y₂O₃-stabilized ZrO₂ tube with porous platinum paste painted inside the closed-end bottom. A platinum wire again served as the lead wire. Another platinum wire contacting the fused Na₂SO₄-NaVO₃ salt solution was used as the working electrode. According to thermodynamic calculations (12), the melt basicity for 900°C was derived from the voltage measured between the two reference electrodes:

\[ E(V) = 1.468 + 0.116 \log a_{Na_2O} \]  

(1)
The oxygen pressure in the melt was determined by the voltage measured between the platinum working electrode and the oxygen probe:

\[ E(V) = 0.039 + 0.0582 \log P_{O_2} \quad (2) \]

Two days after the system reached the internal equilibration at which the oxygen pressure was 1 atm and the melt basicity remained almost constant, samples were taken by quenching small amounts of salt onto a cool alumina rod. The samples of ~0.5g each were put into polyethylene vials which had been cleaned in methanol, dried and weighed. The vials containing the salt samples were weighed to an accuracy of 0.1 mg, and then kept in a desiccator.

The cerium concentrations in the frozen salt samples were determined by neutron activation analysis (NAA) in the Central Irradiation Facility of the Ohio State University Research Reactor. During the irradiation, the target nuclei of Ce-140 absorb thermal neutrons to form Ce-141. The activated Ce-141 nuclei undergo beta decay with the formation of Pr-141 nuclei, which decay further to the ground state by gamma ray emission. The gamma ray emission occurs at 145.43 KeV with a half-time of 33 days for Pr-141. These gamma rays were detected and analyzed with a gamma ray spectrometer.

A series of standard samples with known Ce concentrations was prepared by homogeneously mixing fine Na₂SO₄-10 mol% NaVO₃ salts with CeO₂ powder. The standard samples and the salt samples obtained from solubility experiments were irradiated in the same batch to insure the same irradiation condition.

RESULTS AND DISCUSSION

From the gamma emission for each sample detected and recorded with the gamma ray spectrometer, the specific Ce-141 activities were calculated. The relationship between the specific Ce-141 activities and the Ce concentrations for the standard samples is shown in Fig. 1, which indicates that the specific Ce-141 activities are proportional to the Ce concentrations in the samples, as expected.

Compared to the Ce standards, the Ce concentrations in the salt samples from the solubility experiments were calculated and plotted as a function of melt basicity in Fig. 2. Each datum point in Fig. 2 represents the measured solubility value for a sample from a separate experiment. In Fig. 2, the solubility minimum for CeO₂ in Na₂SO₄-10 mol% NaVO₃ at 900°C occurs at \(-\log a_{Na_2O} = -10.1\) with a concentration of \(-18 \text{ ppm}\) of Ce by weight in the salt solution.
For the basic dissolution of CeO$_2$, the dependence of the solubility on melt basicity is consistent with the dissolution reaction

$$\text{CeO}_2 + \text{Na}_2\text{O} = \text{Na}_2\text{CeO}_3$$

(3)

For excess CeO$_2$, with a henrian proportionality between the activity of Na$_2$CeO$_3$ and its concentration in dilute solutions:

$$\frac{\partial (\log a_{\text{Na}_2\text{CeO}_3})}{\partial (-\log a_{\text{Na}_2\text{O}})} = -1$$

(4)

For the acidic dissolution of CeO$_2$, as discussed in the previous paper (10), the dependence of the solubility upon melt basicity is in agreement with the following dominant dissolution reaction:

$$3\text{CeO}_2 + 4\text{NaVO}_3 = \text{Ce}_3(\text{VO}_4)_4 + 2\text{Na}_2\text{O}$$

(5)

For excess CeO$_2$,

$$\frac{\partial (\log a_{\text{Ce}_3(\text{VO}_4)_4})}{\partial (-\log a_{\text{Na}_2\text{O}})} = \frac{2}{3}$$

(6)

A comparison of the CeO$_2$ solubility in Na$_2$SO$_4$-10 mol% NaVO$_3$ with the solubilities in both pure Na$_2$SO$_4$ and in Na$_2$SO$_4$-30 mol% NaVO$_3$ is made and presented in Fig. 3 (10). The effect of the vanadate anion in stabilizing the acidic solute is obvious, raising the solubility of CeO$_2$ by orders of magnitude. The higher the vanadate anion concentration in the salt solution, the more significant is the observed effect.

The results clearly indicate that the acidic solute of CeO$_2$ in the Na$_2$SO$_4$-NaVO$_3$ solution is cerium orthovanadate, Ce$_3$(VO$_4$)$_4$, instead of cerium sulfate, Ce(SO$_4$)$_2$, as in a pure Na$_2$SO$_4$ melt. This results because the strong acid component V$_2$O$_5$ in the salt solution and its derivatives exhibit higher reactivities with oxide ions than SO$_3$ present in the system.

$$\text{NaVO}_3 + \text{Na}_2\text{O} = \text{Na}_3\text{VO}_4$$

(7)

Thus, according to equation (5) the metavanadate ion reacts with CeO$_2$, leading to the acidic dissolution of the oxide with the formation of the orthovanadate anion. According to the thermodynamic calculations made by Hwang and Rapp (11), NaVO$_3$ is the dominant component containing vanadium and its concentration, or activity, is almost constant in the range of melt basicity concerned in both the previous study (10) and this study, $-9.4 \leq \log a_{\text{Na}_2\text{O}} \leq -13.4$, that is, the range for
the acidic dissolution of CeO$_2$. Equations (5) and (7) provide an explanation for the dependence of the acidic solubility of CeO$_2$ upon solvent basicity, as obtained from the experiments.

The experimentally measured solubilities of CeO$_2$ in Na$_2$SO$_4$-10 mol% NaVO$_3$ are compared to the theoretical predictions (11) in Fig. 5. The two curves for the acidic solubilities are almost the same, but a small deviation for the basic solubilities is observed. This deviation may arise from the difference in activity coefficient for the basic solute in the Na$_2$SO$_4$-NaVO$_3$ solutions with different compositions. In general, the measured solubilities of CeO$_2$ in Na$_2$SO$_4$-10 mol% NaVO$_3$ at 900°C are consistent with the values predicted on the basis of an ideal solution.

The oxide solubility measurements, particularly the comparison of CeO$_2$ solubilities in pure Na$_2$SO$_4$ and in Na$_2$SO$_4$-NaVO$_3$ salt solutions, reinforces the previously described (10) revision to the mechanism of alloy hot corrosion by acidic fluxing postulated by Goebel et al.(13). That model suggested that a strong acid oxide, such as V$_2$O$_5$, MoO$_3$ or WO$_3$ present in sulfate melts, would complex with oxygen anions, thus increasing the melt acidity, namely $P_{SO_3}$. As a result, a protective oxide would experience an increase in its acidic dissolution, and the alloy would undergo severe hot corrosion. That model is based on the assumption that the solubility curve for the oxide remains the same for the pure and mixed sulfate solutions, and that the vanadate causes a significant increase in melt acidity. Although such an analogous explanation is generally valid for aqueous solutions, it is not the case for molten sulfate-vanadate salt solutions.

In spite of the fact that the oxygen anions are indeed strongly complexed to form vanadate anions, the effect is not to reduce the melt basicity, but to increase it. For example, at 900°C, a melt buffered by equal activities of NaVO$_3$ and Na$_3$VO$_4$ assumes a calculated log $a_{Na_2O}$ value of -8.17. Equal activities of V$_2$O$_5$ and NaVO$_3$ occur at a calculated value of -15.33 for log $a_{Na_2O}$. However, a pure Na$_2$SO$_4$ melt equilibrated with 10$^{-3}$ atm SO$_3$ is a very acidic salt with a calculated log $a_{Na_2O}$ = -14.36. In the experimental range of melt basicity, the principal solvent anion of vanadium is the metavanadate, VO$_3^-$, and therefore the oxide ions supplied by oxide dissolution are consumed in forming the orthovanadate anions, VO$_4^{3-}$. Since the cerium solute is incidental to the vanadate reaction, the presence of NaVO$_3$ in Na$_2$SO$_4$ melt would greatly increase the acidic solubility of any oxide. However, the solvent solution is not made more acidic than pure Na$_2$SO$_4$, but more basic. From the previous (10) and the present studies, the solubility minimum for CeO$_2$ at 900°C lies at log $a_{Na_2O}$ = -11.7 for pure Na$_2$SO$_4$, -10.1 for Na$_2$SO$_4$-10 mol% NaVO$_3$, and -9.4 for Na$_2$SO$_4$-30 mol% NaVO$_3$, respectively. These results agree...
quantitatively with the theory of Hwang and Rapp (11) based on an ideal solution for the solutes.

In their study, Jones et al. (7) observed an increase in the reactivity for the oxides Y₂O₃, CeO₂, and ZrO₂ with salt solutions in the order of V₂O₅ > NaVO₃ > Na₃VO₄, i.e. with increasing salt acidity. Seiersten and Kofstad (14) studied the hot corrosion of MCrAlY coatings on Inconel 600 alloy by NaVO₃−V₂O₅ salt solutions at 650-800°C and found that the corrosion rate increased with increasing V₂O₅ content. In an investigation of the leaching of Y₂O₃ from yttria-stabilized zirconia by Na₂SO₄−NaVO₃ melts at 900°C, Nagelberg (3) reported that the parabolic rate constant for the hot corrosion attack was proportional to the SO₃ pressure and the square of NaVO₃ concentration. In the measurement of thin film salt chemistry during hot corrosion of preoxidized nickel, Otsuka and Rapp (15) noticed that NaVO₃ added to Na₂SO₄ enhanced the onset of hot corrosion and substrate sulfidation. The solubility measurements reported here as well as in the previous paper (10) are consistent with all these results and observations.

CONCLUSIONS

From the experimental results and discussion above, the following conclusions can be drawn.

1. The oxide CeO₂ dissolves in Na₂SO₄−10 mol% NaVO₃ salt solution at 900°C either as a basic solute, Na₂CeO₃, or as an acidic solute, Ce₃(VO₄)₄, with a solubility minimum occurring at log a₀₂₀ = -10.1.

2. The CeO₂ solubilities experimentally determined are consistent with the theoretically predicted dependence of the oxide solubility upon the NaVO₃ content in the Na₂SO₄−NaVO₃ salt solutions. Even a small vanadate concentration raises the acid solubility of any oxide significantly.

3. The solubility measurements show that solutions of the salts of strong acids with a Na₂SO₄ solvent provide higher acidic solubilities for all oxides. The mixed salt solutions are generally buffered to higher values of basicity. The results agree quantitatively with a theory based on the "common component effect". The sodium oxide activity is tied to both CeO₂ dissolution and to equilibria among vanadate species, so these equilibria are interdependent.

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Figure 1: Specific Ce-141 activity vs. Ce concentration for standard samples.

Figure 2: Solubility of CeO₂ in Na₂SO₄ - 10 mol% NaVO₃ at 900°C and 1 atm O₂.

Figure 3: Measured solubilities of CeO₂ in fused salts at 900°C.

Figure 4: Measured and calculated solubilities of CeO₂ in Na₂SO₄ - 10 mol% NaVO₃ at 900°C.