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METAL OXIDE SOLUBILITY AND MOLTEN SALT CORROSION. (U)
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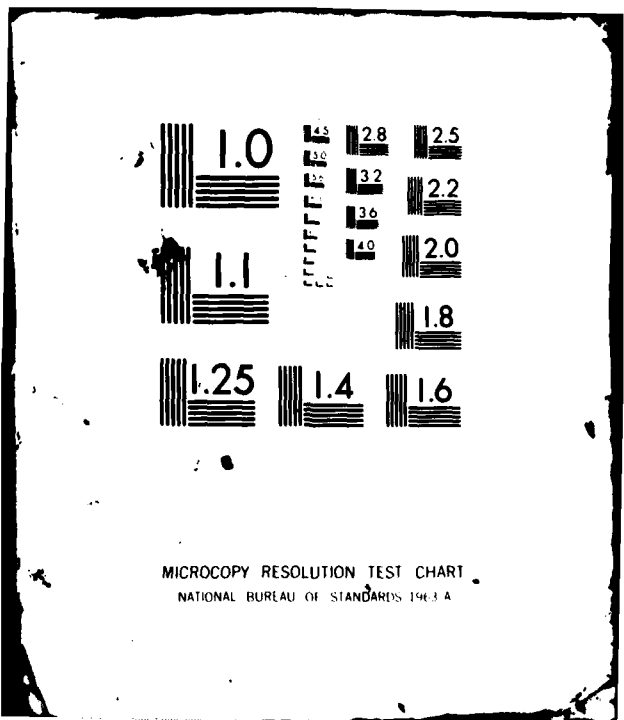
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20. ABSTRACT (Continued)

(SO₂ and SO₃) of the gas phase. The melt acidity at the solubility minimum of NiO, Y₂O₃, and CoO is nearly the same, but differs by a factor of 10⁵ for Al₂O₃ and Cr₂O₃. Alumina is most protective in basic melts, chromia in acid melts. Maximum corrosion protection is achieved by operating at the solubility minimum of the protective oxides.

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METAL OXIDE SOLUBILITY AND MOLTEN SALT CORROSION

I. INTRODUCTION

Molten salt corrosion of metals has been a technological problem at least since the 1940's, when the attack of molten salts and slags on boiler tubes in coal-fired steam-generating plants was noted^{1,2}. Since then, the adverse impact of this kind of corrosion has continued to grow as more technologies operate at high temperatures in environments where they are exposed to molten salts. Among such technologies are: gas turbines^{3,4,5}, coal gasification⁶, MHD^{7,8}, fluidized bed combustion, molten salt fuel cells, salt processing baths, and solar energy storage by molten salts.

Although corrosion research in these areas is being carried out, the work tends to be oriented toward specific technologies rather than toward the basic phenomena underlying all of them. Consequently, workers are frequently unaware of relevant progress in fields other than their own. A general review of molten salt corrosion chemistry was published recently⁹. In the present paper, one of the phenomena, the solubility of metal oxides in molten salts, is discussed in terms of its importance to the understanding of molten salt corrosion.

II. PROTECTIVE COATINGS

Since most structural metals and alloys are not sufficiently corrosion-resistant toward molten salts, they are usually coated with alloys having a substantially higher corrosion-resistance. Metals commonly used as alloy constituents include cobalt, nickel,

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chromium, aluminum, and yttrium. (Commonly used alloys are frequently referred to by acronyms, e.g., CoCrAlY, NiCrAlY.) For a particular set of constituents, the relative concentrations are adjusted to optimize coating properties for the application of interest. The protective power of the coating derives from the formation of an adherent and corrosion-resistant oxide layer on top of the coating, and the metal composition is chosen so that after air oxidation, the protective properties are optimized.

One of the factors which affects the corrosion resistance of the oxide layer is the solubility of the individual oxides in the molten salt. Since this solubility is best discussed in terms of the equilibria between the solid oxide and the melt constituents, the principles involved are briefly discussed in the next section.

III. ACID-BASE EQUILIBRIA AND OXIDE SOLUTION RELATIONS IN MOLTEN SALTS

For this discussion it is convenient to separate salts into two classes, analogous to a similar division for molecular solvents used at ambient temperatures. (A) The first class includes salts like the alkali halides which function as pure solvents, i.e., they do not participate in the solute equilibria. (B) The second group includes oxyanion salts which, since the work of Lux¹⁰ and Flood¹¹, have been considered in terms of the equilibrium



in which the oxide ion (O^{2-}) plays a role quite analogous to the

hydrogen ion in aqueous solution. For example,



The significance of these equilibria for oxide solubility is that the basicity of the melt, and consequently the metal ion concentration, is directly affected by the gas composition in equilibrium with the melt.

The simplest solubility behavior is that exhibited by, for example, an alkali earth oxide in an alkali halide



The solubility product is defined as

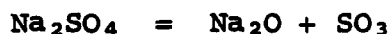
$$K_{\text{sp}} = [\text{Ba}^{2+}] [\text{O}^{2-}] \quad (1)$$

where the quantities in brackets may represent thermodynamic activities* or concentrations on any convenient scale. However, if comparison is to be made with the results of thermodynamic calculations, the standard state of the pure solid, BaO in this case, must be taken into account. Since the activity is taken as unity for the pure solid, the concentration and activity must be expressed on a mole fraction scale.

The concentration of the metal ion in solution is dependent on the basicity of the melt, just as the solubility of a hydroxide in aqueous solution is pH-dependent. By analogy with pH, the melt basicity is commonly expressed as $\text{pO}^{2-} = -\log a_{\text{O}^{2-}}$.

* To avoid single ion activities, the neutral species must be used, e.g., $K_{\text{sp}} = a_{\text{BaCl}_2} \cdot a_{\text{Na}_2\text{O}}$ in a NaCl melt.

In an alkali halide solvent, pO^{2-} can only be altered by adding a soluble oxide like Na_2O . In an oxyanion solvent, however, the metal ion solubility can also be altered by changing the gas phase composition. For example, the acid-base equilibrium for Na_2SO_4 is



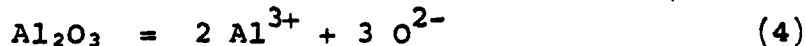
$$K_e = [Na_2O]P_{SO_3} \quad (2)$$

Thus, by fixing P_{SO_3} , $[Na_2O]$ (or $[O^{2-}]$) will be fixed and this in turn fixes $[Ba^{2+}]$, i.e., from (1) and (2)

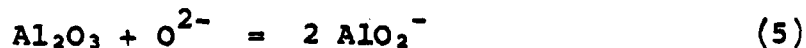
$$[Ba^{2+}] = (K_{sp}/K_e)P_{SO_3} \quad (3)$$

Note, however, that $[Ba^{2+}]$ will be "controlled" by P_{SO_3} only when $K_{sp} < K_e$. For example, taking the known values of K_{sp}^{12} and K_e^{13} , $\sim 10^{-4}$ and $\sim 10^{-14}$, respectively, leads to $[Ba^{2+}] = 10^{10} P_{SO_3}$. Thus for any plausible values of P_{SO_3} , the melt will not be buffered against the addition of the oxide, pO^{2-} will be determined by the solubility of the added oxide alone, and the oxyanion solvent behaves, in this respect, like an alkali halide. It is only for very slightly soluble oxides that relations like eq. (3) are significant.

The oxides of several metal oxides have been found to be amphoteric, i.e., their solution reactions are pO^{2-} -dependent. As pointed out by Stroud and Rapp¹⁴, Al_2O_3 dissolves in "acid" melts according to

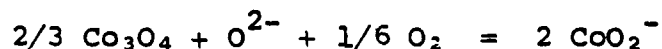
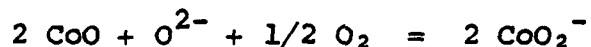
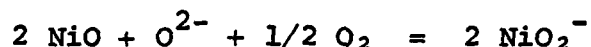
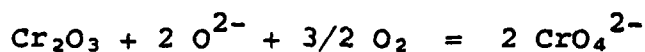


whereas in "basic" solution



The particular value of pO^{2-} which characterizes the transition from "acid" to "basic" appears to be a function of the oxide solute, rather than of the solvent. Similar behavior has been observed for Y_2O_3 ¹⁵. In oxyanion solvents, the solubility, measured as $[Al^{3+}]$ or $[AlO_2^-]$, can be controlled by controlling the gas pressure, e.g., SO_3 for a Na_2SO_4 melt. In an alkali halide melt, pO^{2-} can be fixed independently by adding a soluble oxide, such as Na_2O .

In contrast to Al_2O_3 and Y_2O_3 , in which the metal ion has a single valence in both its acid and basic forms, several transition metal oxides require a valence change for the basic solution reactions:



In these cases, the solubility depends not only on pO^{2-} , but also on the oxygen pressure.

IV. METHODS FOR DETERMINING SOLUBILITIES

A. Thermodynamic calculations

In order to calculate solubilities of oxides, equations such as (1) must be recast in a form containing only neutral species, since it is only for these that thermodynamic values exist. This means including the solvent explicitly in the equation. Thus for the solubility of BaO in $NaCl$



and

$$K_{\text{sp}}^{\text{a}} = a_{\text{BaCl}_2} \cdot a_{\text{Na}_2\text{O}} \quad (7)$$

since the activity of solid BaO is unity by definition, and is nearly unity for the solvent in dilute solution. The major obstacle to carrying out such calculations is the lack of needed data.

In order to compare thermodynamic equilibrium constants with experimental values, activity coefficients for the solute species are required:

$$a_i = \gamma_i X_i \quad (8)$$

where γ_i is the activity coefficient and X_i the mole fraction of species i .

The activity coefficient of Na_2O in NaCl and Na_2SO_4 has been determined^{16,17} and is of the order 10^{-4} . Thus equilibrium constants in terms of activities and concentrations are expected to differ by several orders of magnitude. Only rarely are activity coefficients available for solute species of interest to corrosion chemistry, and therefore constants on the two scales generally cannot be compared for consistency. However, in cases like reaction (1), a knowledge of the thermodynamic and concentration constants can be used to generate activity coefficients of solute species such as BaCl_2 :

$$K_{\text{sp}}^{\text{a}} = (\gamma_{\text{BaCl}_2} \cdot X_{\text{BaCl}_2}) \cdot (\gamma_{\text{Na}_2\text{O}} \cdot X_{\text{Na}_2\text{O}})$$

$$K_{\text{sp}}^{\text{x}} = X_{\text{BaCl}_2} \cdot X_{\text{Na}_2\text{O}}$$

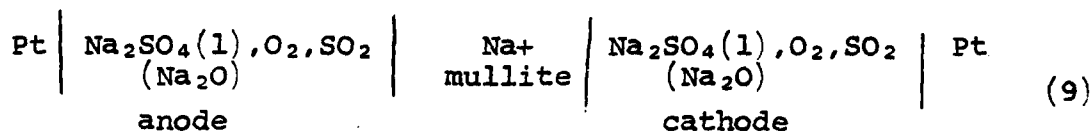
$$K_{\text{sp}}^{\text{a}} / K_{\text{sp}}^{\text{x}} = \gamma_{\text{BaCl}_2} \cdot \gamma_{\text{Na}_2\text{O}}$$

B. Experimental Methods

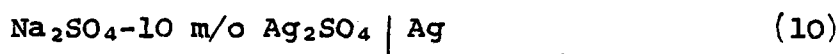
The simplest and oldest method for determining oxide solubility is to equilibrate the oxide in the salt and chemically analyze samples of the melt, generally by solution in water and using standard analytical methods. This method assumes that all the material dissolved in the melt is also soluble in water. If the solubility is fairly high, reasonably accurate values of the metal ion concentration can be obtained. Similarly, the oxide concentration can be determined by titration with standard acid.

The most comprehensive study of this type was carried out by Voskresenskaya and Kashcheev¹², who measured the solubility of BaO, CaO, MgO, ZnO, Cr₂O₃, and CuO in molten LiCl, NaCl, KCl, Li₂SO₄, and Na₂SO₄ at 100° intervals from 700 to 1200°C, relying primarily on acid titration of the melt. Although an attempt was made to keep the melt under nitrogen, primarily to protect the nickel crucible, it is not possible to know the oxygen pressure, which would influence the basic solubility of Cr₂O₃.

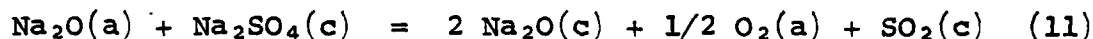
More recently it has been recognized that, since the oxide solubility is pO^{2-} -dependent, both the metal ion and O^{2-} must be measured. Rapp and coworkers^{14,18} have used potentiometry to determine the oxide activity, and chemical analysis to determine the metal concentrations for Al₂O₃, Cr₂O₃, NiO, and Co₃O₄ in molten Na₂SO₄ at 1200 K. In one version¹⁴, the oxide activity was measured with the cell



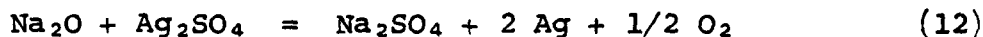
The cathode compartment, which serves as the reference electrode, is enclosed in a mullite tube isolating the reference melt and gas supply from the anode compartment in equilibrium with the solid oxide whose solubility is being measured. In another version, the reference electrode used was



in a mullite tube. This electrode is easier to handle since no gases are involved. The reaction for cell (9) is



where (a) and (c) designate anode and cathode, respectively, whereas with reference electrode (10)



The oxide activity in the cathode compartment was set by fixing the presence of SO_2 and O_2 . Melt samples were taken from saturated melts at various fixed oxide activities and analyzed by atomic absorption (after solution in water) which measures the dissolved material in both acid and basic forms. As an illustration, the solubility of NiO in Na_2SO_4 as a function of $a_{\text{Na}_2\text{O}}$ is shown in figure 1. The nature of the solution reactions was confirmed by the agreement of the slopes expected from the solution reaction with the experimental slopes. For the acid solution



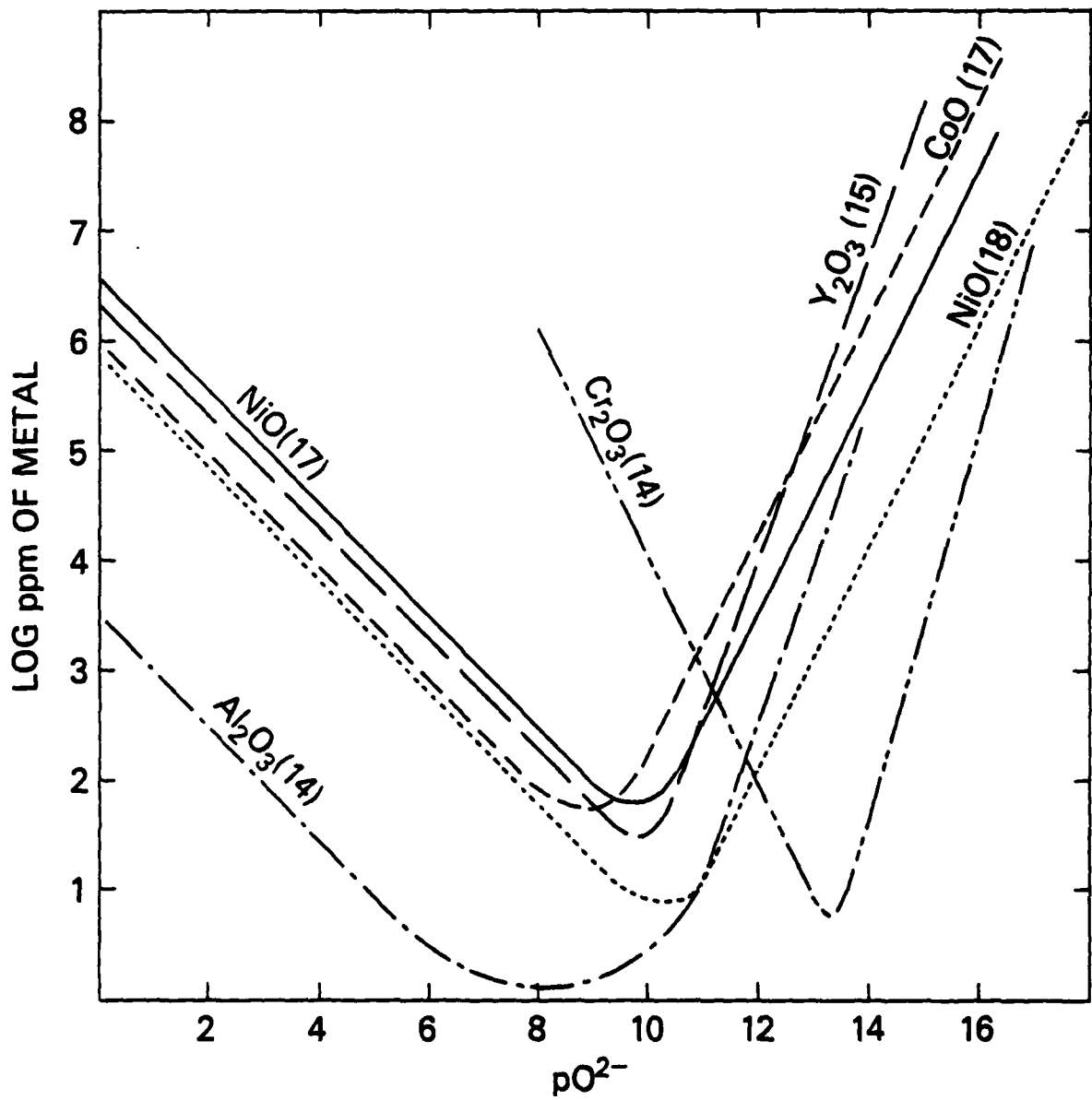
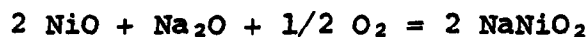


Fig. 1 — Solubility of oxides in Na₂SO₄ at 1200K as function of pO²⁻

for which $[\partial(\log a_{\text{NiSO}_4}) / \partial(-\log a_{\text{Na}_2\text{O}})] = 1$.

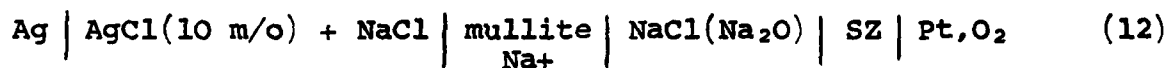
For the basic solution



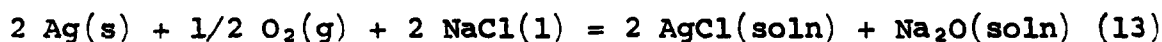
where $[\partial(\log a_{\text{NaNiO}_2}) / \partial(-\log a_{\text{Na}_2\text{O}})]_{\text{O}_2} = -1/2$

and $[\partial(\log a_{\text{NaNiO}_2}) (\partial(\log P_{\text{O}_2}))]_{a_{\text{Na}_2\text{O}}} = -1/4$

Additionally, NaNiO_2 was found by X-ray diffraction of the quenched melt. A similar method was used by Deanhardt and Stern¹⁹ to measure the solubility of Mn_2O_3 in NaCl at 1100 K and Mn_3O_4 in Na_2SO_4 at 1200 K, except the indicating electrode was stabilized zirconia (SZ) which is reversible to $a_{\text{Na}_2\text{O}}$ in the melt, and to O_2 in the gas phase. For example, in NaCl , the cell employed is



for which the cell reaction is



For this cell, only a single oxygen pressure needs to be maintained and the oxide activity can be changed by the addition of a soluble oxide to the melt.

A coulometric titration method which avoids the long equilibration time and chemical analyses required by the above method was recently developed by Deanhardt and Stern²⁰. In this method, the metal ion is added as a soluble salt, e.g., NiCl_2 in NaCl . Oxide ion is generated coulometrically, using a titration cell consisting of a second SZ electrode combined with a counter

electrode. By applying a voltage to this cell, the reaction



is driven to the right, producing oxide ions in the melt where they react with the metal ion or metal oxide. From a knowledge of the initial metal ion concentration, the charge Q passed, and the emf of cell, the acid and basic equilibrium constants can be calculated by regression analysis, using equations developed by the authors¹⁷. In addition, the analysis also yields the oxide-peroxide equilibrium constant for the reaction



which occurs^{21,22,23,24} in oxide-containing melts. Depending on what activity coefficients are available, the equilibrium constants may be expressed on an activity or concentration scale. A typical titration curve can be obtained in ~24 hours, data (Q and emf) being recorded automatically with a data logger.

V. RESULTS

A. Solution Reactions

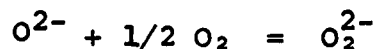
For alkali metal and alkali earth oxides, the solution reactions are straightforward, since they are independent of pO^{2-} . For alkali metal oxides, they are of the form



and for the alkaline earth oxides



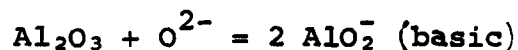
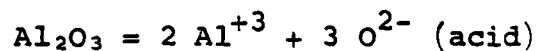
In addition, for all oxides in the presence of oxygen, O^{2-} is in equilibrium with O_2^{2-} (peroxide) and O_2^- (superoxide):



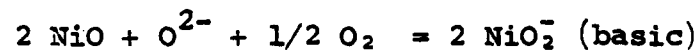
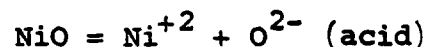
Equilibrium constants for these reactions depend primarily on the major melt cation and the temperature. For example, in NaNO_3 near 500°C , O^{2-} is virtually absent^{21,22}. In molten NaCl and Na_2SO_4 , only the $\text{O}^{2-}-\text{O}_2^{2-}$ equilibrium is significant^{23,24}.

We next list the acid and basic solution reactions for oxides which have been studied so far:

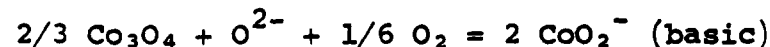
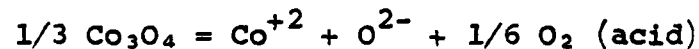
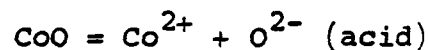
Aluminum¹⁴:



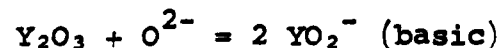
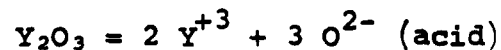
Nickel^{17,18}:



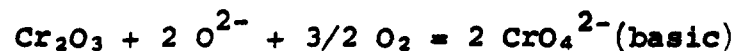
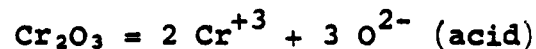
Cobalt^{17,18}:



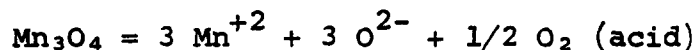
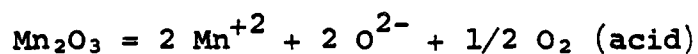
Yttrium¹⁵:



Chromium¹⁴:



Manganese¹⁹:



The basic solution reactions of the manganese oxides have not yet been studied, but most likely produce MnO_4^- (permanganate) in solution.

All of the above solution reactions are based on studies in molten Na_2SO_4 and/or NaCl at temperatures in the 1100-1200 K range. So far, the list of oxides studied and of interest to corrosion science is not long. In figures 1* and 2, the solubility of the metal oxides (sum of soluble species in both acid and basic forms) is shown in Na_2SO_4 and NaCl , respectively, as a function of $p\text{O}^{2-}$. A $p\text{O}^{2-}$ scale can be converted to $-\log$ mole scale fraction oxide by subtracting 3.35 from $p\text{O}^{2-}$ on the Na_2SO_4 scale and 3.77 on the NaCl scale. It should be emphasized that, because more than one equilibrium contributes to the solubility curve, there is no simple relation between the metal and oxide concentration at the minimum. This is illustrated in Table I.

*Very recent work by Pullockaran and Rapp²⁵ indicates that the curves for Al_2O_3 and Cr_2O_3 in figure 2, although correct in shape, are seriously off in position. The position of the new minima of the curves are: $\text{Al}_2\text{O}_3 - p\text{O}^{2-} = 15.5$, $\log \text{ppm metal} = 1.1$; $\text{Cr}_2\text{O}_3 - p\text{O}^{2-} = 16.0$, $\log \text{ppm metal} = 2.5$.

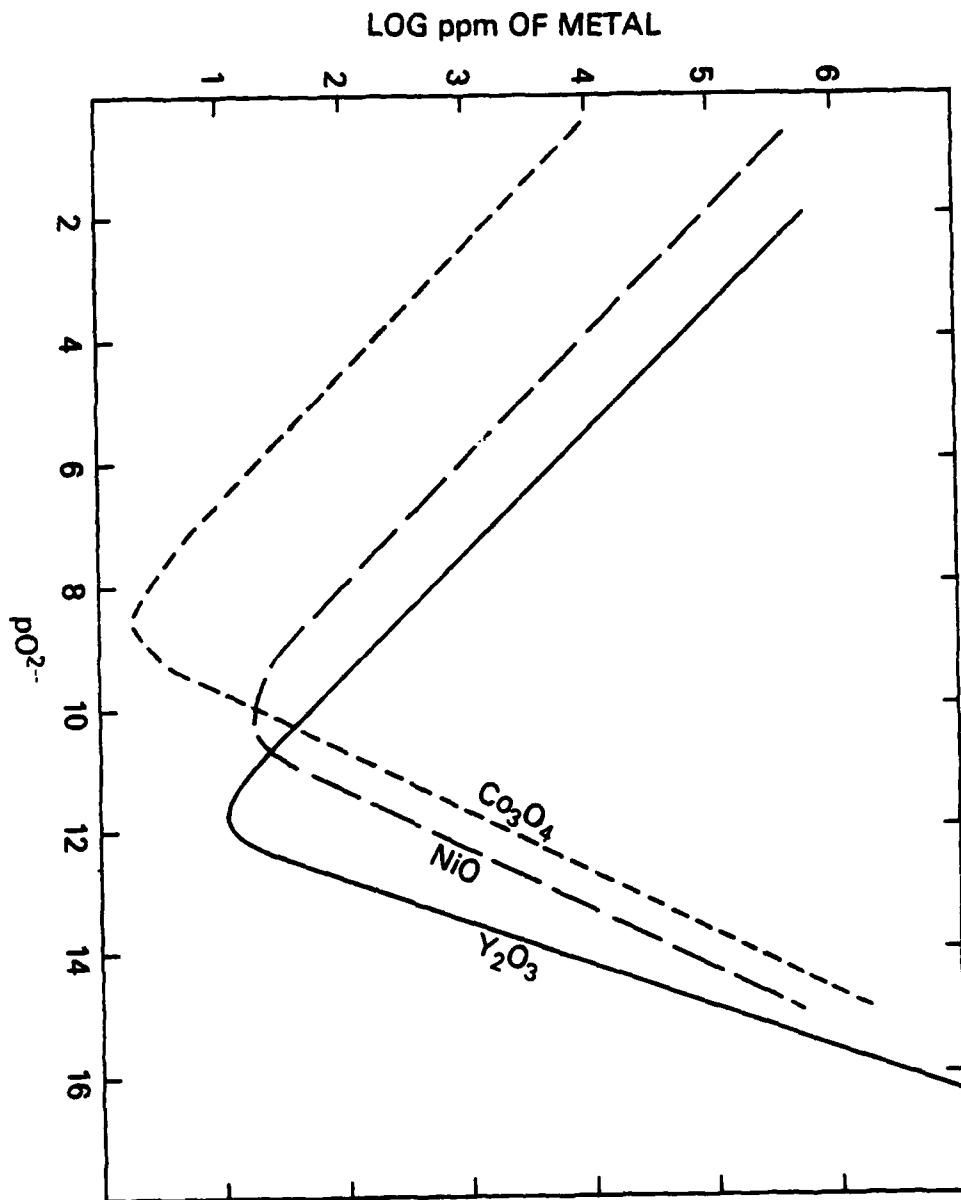


Fig. 2 - Solubility of oxides in NaCl at 1100 K as function of pO₂

TABLE I
Metal and Oxide Concentration at the Solubility Minimum
in Na₂SO₄

<u>Cxide</u>	<u>Soluble Metal (X_M) min</u>		<u>X_{Na₂O}(min)</u>	<u>Reference</u>
	<u>Acid</u>	<u>Basic</u>		
NiO	1.71x10 ⁻⁵ (total)		7.08x10 ⁻⁸	18
NiO	9x10 ⁻⁵	12.7x10 ⁻⁵	5.58x10 ⁻⁷	17
CoO	6.8x10 ⁻⁵	25.2x10 ⁻⁵	2.22x10 ⁻⁶	18
Y ₂ O ₃	2.9x10 ⁻⁶	5.6x10 ⁻¹⁵	4.42x10 ⁻⁷	15
Al ₂ O ₃	5.26x10 ⁻⁷ (total)		7.6x10 ⁻⁶	14
Cr ₂ O ₃	1.53x10 ⁻⁶ (total)		1.11x10 ⁻¹⁰	14

B. Solubility Data

Solubility data may be presented in several ways: (1) Equilibrium constants on either a concentration or activity scale can be given for the acid and basic solution reactions. These constants can be interconverted if the activity coefficients of all species in solution are known. (2) Metal concentrations in solution may be given (usually graphically) as a function of oxide activity or concentration. (3) The "solubility" of the stoichiometric oxide may be given in a solvent, nominally "neutral," in which the oxide activity is not known. All of these methods have been used, but they can only be compared if enough auxillary data, such as activity coefficients, are available. Fortunately, such comparisons are possible for most of the structural metals of interest to corrosion scientists. Nearly

all of these studies are the work of Rapp and coworkers^{14,18,25} and of Deanhardt and Stern^{15,17}.

The principal results from these latter works are collected in figures 1 and 2 where the oxide solubilities are given in ppm soluble metal as a function of pO^{2-} in both NaCl at 1100 K and Na_2SO_4 at 1200 K.

VI. SOLUBILITY AND CORROSION

We consider next the implications of these solubility plots for corrosion science. The major point evident in figures 1 and 2 is that, whereas the solubility minima of the metals studied do not vary widely, all being under 100 ppm, they do fall at distinctly different points on the pO^{2-} scale. Moreover, the solubilities are strongly affected by the melt pO^{2-} , and can reach 100,000 ppm or more for only 2-3 pO^{2-} units change. To minimize corrosion caused by the dissolution of metal oxides in the melt, one should therefore seek to operate near the solubility minima, either by employing appropriate metals or by adjusting the pO^{2-} of the molten salt.

For static applications with bulk metals, as in molten salt batteries or salt baths used in various technologies, it may be possible to adjust pO^{2-} by the addition of basic oxides. Such an adjustment is not difficult, particularly if the alloy composition has been chosen so as to achieve the solubility minima for all the alloy components. Where these lie in a narrow range of pO^{2-} , as is the case for NiO, CoO, and Y_2O_3 , this presents no problem. For oxyanion salts, it may also be possible to control

pO^{2-} by maintaining a fixed concentration of the conjugate gas (SO_3 , CO_2 , etc.) over the melt.

Even in salt corrosion problems which are not static or where the salt pO^{2-} cannot be directly controlled, the understanding gained from solubility studies has useful application. More effective methods for reducing hot corrosion of gas turbines, for example, can be developed when more precise oxide solubility minima and solubility conditions are determined, understood, and applied. Hot corrosion results from deposition on the turbine blades of molten sulfate films which, because of the relatively clean fuels and high temperatures involved, tend to be predominantly Na_2SO_4 . Gas turbine gases also contain SO_3 at partial pressures of approximately 10^{-6} to 10^{-4} atm depending on the fuel sulfur content. Assuming equilibrium to exist between the gas and sulfate deposit, one may predict the a_{Na_2O} (or pO^{2-}) expected in the molten salt film by substituting these P_{SO_3} values into the Na_2SO_4 dissociation reaction:



where, at $1200^\circ K$,

$$K = a_{Na_2O} \cdot P_{SO_3} \approx 10^{-18}$$

The resultant predicted pO^{2-} range is 12 to 14; that is, significantly on the acidic side of the pO^{2-} scale. At these pO^{2-} values, Cr_2O_3 is the least soluble oxide (Fig. 2), and Cr_2O_3 -forming alloys therefore should be most resistant to hot corrosion. In general this is true, especially in comparison with NiO- or CoO-forming alloys, whose minima lie between 9 and

10.5 and which show high solubilities in the pO^{2-} range of 12 to 14.

The comparison of Cr_2O_3 with Al_2O_3 behavior, however, is ambiguous. In the original work by Stroud and Rapp¹⁴, Al_2O_3 was reported (as indicated in Fig. 2) to have minimum solubility at 8.5, whereas Cr_2O_3 had minimum solubility at 13.5 pO^{2-} , suggesting a marked difference in their behavior, Al_2O_3 supposedly more resistant to basic melts and Cr_2O_3 more resistant to acidic melts. Recently, however, Pullockaran and Rapp²⁵ have corrected these results, shifting both the Al_2O_3 and Cr_2O_3 minima in the acidic direction, Al_2O_3 to 15.5 and Cr_2O_3 to 16.0 pO^{2-} . Thus, Al_2O_3 -forming alloys would be expected to be equal, or even superior, to Cr_2O_3 -forming alloys against "normal" hot corrosion. However, field experience and burner rig tests²⁶ indicate that Cr_2O_3 formers are generally more resistant to hot corrosion than Al_2O_3 formers.

There are several factors which contribute to the discrepancy between solubility studies and field results. First, the assumption that the turbine blade sulfate is adequately simulated by pure Na_2SO_4 , and that its basicity is controlled solely by interaction with combustion gas SO_3 , is only an approximation. Reaction of the sulfate with the turbine blade metal is well known to affect the acid-base chemistry of the melt²⁷. For example, the sulfate reactions which lead to metal sulfide formation in the blade metal tend to increase the O^{2-} concentration in the remaining surface salt. This can result in basic dissolution of the surface oxides, i.e., "basic fluxing" hot

corrosion, particularly under high turbine temperature-low SO_2 conditions. In addition, it would be intuitively expected that as other cations or salts are incorporated in the molten surface phase, the solubility of a given metal oxide in that melt would change. Some indications, e.g., of the interactions affecting solubility for Co, Ni, Na ternary sulfates have recently been obtained²⁸. Efforts to relate the solubility of protective oxides in molten Na_2SO_4 to the corrosion of gas turbines are very much hampered by the difficulty in defining hot corrosion conditions and the resultant Na_2O activities in the surface salt melts.

A second contributing factor is that the solubility behavior of a bulk oxide may be different from that of a thin film of the same oxide existing on a metal substrate. In aqueous systems, for example, although stripped iron oxide films resist dissolution in strong acids, they are readily dissolved by reductive dissolution when the exposure takes place while they are still on the metal²⁹. The possible operation of a similar "reductive dissolution" mechanism in salt systems may be a factor in the discrepancy noted above.

Finally, other properties of the oxide film beyond simple solubility undoubtedly affect its hot corrosion performance. These include such properties as surface oxide integrity, adherence, and diffusivity and growth characteristics. The deleterious effect of NaCl in disrupting surface oxide integrity so as to promote oxidation and hot corrosion is well documented³⁰. Similarly, yttrium is widely accepted as improving the hot

corrosion performance of MCrAlY (M = Co, Ni or Fe) turbine blade coatings by increasing the adherence of the Al₂O₃ film formed on the MCrAlY surface³¹. The morphology of hot corroded metals also often shows discrete, repeated oxide layers, suggesting that in some cases attack may involve alternate formation and penetration of, and then corrosion beneath, "protective" oxide layers.

Thus oxide solubility does not solely determine the salt corrosion resistance conferred by metal oxides. Nonetheless, "insolubility" is a fundamentally required property of corrosion-resisting oxides; oxides which are excessively soluble, either inherently or because they are used in the wrong pO₂⁻ range, can never provide metal protection. The great benefit of recent solubility studies has been to establish the quantitative relation between oxide solubility and melt pO₂⁻ for Cr₂O₃, Al₂O₃ and other oxides critical in high temperature technology. Further solubility studies, based on the methodologies now developed, could prove of significant aid in improving metal performance in molten salts, for example, by (i) screening new potentially protective oxides, (ii) exploring the solubility of metal oxides in mixed composition salts (the more realistic field situation), or (iii) elucidating oxide-salt behavior in other technological systems, e.g., coal gasification.

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