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Low Quality Fuel Problems with Advanced Engine Materials

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The ultra high-power, high-efficiency engines of the future will utilize advanced materials including ceramics, composites, and augmented metals. In many cases, these materials may be subject to corrosion by high temperature gases and molten salt deposits resulting from contaminants (e.g., sodium, sulfur, vanadium) in the fuel or engine air. This Memorandum Report gives a short overview of the state of knowledge that exists today concerning corrosion of ceramics and metals by fuel contaminants, and of possible new avenues for research and materials development. It was originally presented as the Keynote Paper for the Session on Hot-Corrosion, Combustion, and Emissions at the DOE-sponsored Coatings for Advanced Heat Engines Workshop, July 27-30, 1987, Castine, ME.				
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LOW QUALITY FUEL PROBLEMS WITH ADVANCED ENGINE MATERIALS

INTRODUCTION

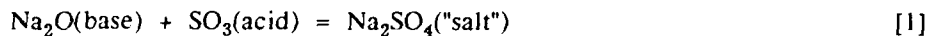
As petroleum resources diminish, the future will bring strong incentives for the use of low quality fuel in engines employing advanced materials. In its present usage, the term "advanced materials" refers principally to the ceramics, silicon carbide (SiC), silicon nitride (Si_3N_4), and stabilized zirconia (ZrO_2); to high-chromium content, silicon-augmented, or specially processed metals; and to ceramic-fiber reinforced metals or ceramics. Other ceramics such as mullite, Ca_2SiO_4 , CaTiO_3 , ZrSiO_4 , and ZrTiO_4 have been suggested for engine usage, but these are as yet little developed.

Of the contaminants occurring in low quality fuel, experience to date has indicated that sodium, sulfur, vanadium, phosphorus, and lead are the most likely to cause degradation of the advanced materials projected for future engines.

This review is organized therefore to first look briefly at how these contaminants, especially vanadium, react in the molten salt corrosion of metals, and then to examine how the same contaminants react in the molten salt degradation of ceramics.

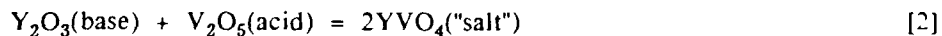
ACID-BASE REACTIONS OF OXIDES

During combustion, fuel contaminants are converted to oxides such as Na_2O , SO_2 - SO_3 , V_2O_5 , etc. which have strong acid-base characteristics. These oxides corrode metals and ceramics by acid-base reactions with the ceramic oxides or the protective oxide scales formed on the metal or ceramic surface (e.g., SiC and Si_3N_4 rely on a SiO_2 surface layer for high temperature stability in air). When molten salt deposits are present, the acid-base reactions are often best treated by the Lux-Flood (1) theory where the various molten salt compounds are described by reversible reactions such as



and the activities of the acidic and basic components in the melt are fixed by the dissociation constant of the reaction (e.g., $10^{-16.7}$ for reaction [1] at 1200°K , cf. ref. 6).

In solid state oxide reactions, the Lewis theory, which defines acid-base behavior in terms of the ability of the species to donate (base) or accept (acid) electrons, is the more useful. This allows, for instance, ready understanding of reactions of the type

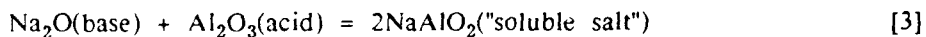


An excellent insight into the influence of Lewis acid-base character in determining oxide reactions is provided by the works of Duffy (2,3) on silicate glass and other oxide systems.

VANADIC HOT CORROSION OF METALS

Since metal engines (with metallic coatings) will be in use for many years to come, the first "new" low quality fuel problem, as the vanadium level in the world's oil supplies rises, is likely to be molten vanadate corrosion of metals. Before discussing vanadic hot corrosion, however, it is beneficial to review some aspects of molten sulfate hot corrosion.

Molten sulfate corrosion has been studied extensively, and acid-base oxide reactions, although certainly not the only critical reaction in sulfate hot corrosion, have been shown to be important. Initiation of corrosive attack at 900°C (i.e., in the so-called "high temperature" hot corrosion regime) appears often to involve "basic" fluxing of the protective surface oxide, e.g.,



where the Na_2O activity in the molten sulfate deposit has been raised by metal sulfide formation (4). Similarly, in 700°C "low temperature" hot corrosion, acidic fluxing of cobalt oxide by SO_3 in the turbine gas is the apparent cause of attack (5).

Acid-base oxide reactions with molten sulfate have been examined by Rapp (6) through the measurement of oxide solubilities as a function of Na_2O activity in fused Na_2SO_4 (Fig. 1). Fig. 1 shows clearly the influence of Na_2O activity on oxide solubility. It also serves to rank the acid-base character of the individual oxides. For example, cobalt oxide has the least acidic nature of the oxides in Fig. 1 and reacts as an acid with Na_2O (forming sodium cobaltate) only for Na_2O

activities above $10^{-9.3}$. At lower Na_2O activities (i.e., when the Na_2SO_4 melt becomes more acidic as the SO_3 activity increases), Co_3O_4 acts as a base, producing cobalt sulfate. Conversely, Al_2O_3 and Cr_2O_3 are substantially more acidic and continue to react as acids forming sodium chromate and sodium aluminate until the SO_3 activity exceeds $10^{-1.2}$ (equivalent to an Na_2O activity of $10^{-15.5}$), and only then begin to act as bases.

The data for SiO_2 in Fig. 1 illustrate a third important factor--that all oxides may not follow this simple acid-base reaction behavior. Although other work indicates that sodium silicate would be produced at higher Na_2O activities, only physical solubility of SiO_2 (with no evidence of reaction with either Na_2O or SO_3) was found by Rapp over the activity range indicated in Fig. 1. No explanation has been given, but, as noted by Duffy (3), "network forming" oxides such as SiO_2 (also B_2O_3 and P_2O_5) may possess lattice bonding energies that can override weak acid-base driving forces.

Compared to molten sulfate corrosion which involves only Na_2SO_4 , vanadic hot corrosion appears potentially more complex because five compounds (Fig. 2), ranging from high V_2O_5 -activity $\text{Na}_2\text{V}_{12}\text{O}_{31}$ to high Na_2O -activity Na_3VO_4 , exist in the Na,V,O system. There has also been substantially less research of vanadic hot corrosion (particularly relating to gas turbine alloys and coatings). As a result, uncertainty still remains on such questions as:

- 1) which vanadate compound is most corrosive,
- 2) what is the role of sulfur (or SO_3) in vanadic corrosion,
- 3) can V_2O_5 inhibit sulfate-induced hot corrosion, and
- 4) do sulfate and vanadate corrosion mechanisms differ fundamentally?

Early investigations of vanadic corrosion of gas turbine alloys (mostly Ni-based) usually found $\text{Na}_2\text{V}_{12}\text{O}_{31}$, the most acidic vanadate, to be most corrosive, and Na_3VO_4 to be essentially innocuous. A diametrically reversed ranking was observed in a recent study (7) of vanadic attack on a 35 wgt-% chromium CoCrAlY blade coating alloy where Na_3VO_4 , the most basic vanadate, was most corrosive. Both results are reconcilable, however, by Fig. 1 which makes it understandable that nickel-based alloys with relatively basic NiO surface oxides would react most readily with acidic $\text{Na}_2\text{V}_{12}\text{O}_{31}$, whereas acidic Cr_2O_3 -rich 35-% chromium CoCrAlY would react most strongly with basic Na_3VO_4 . Which vanadate is "most corrosive", at least in initiation of attack, will depend thus on the nature of the oxide on the metal surface.

When sulfur is also present in the fuel, interactions will occur between the vanadium and sulfur species. For example, V_2O_5 has been reported to inhibit Na_2SO_4 hot corrosion of nickel by formation of a refractory (mp. 1210°C) $\text{Ni}_3(\text{VO}_4)_2$ layer on the nickel surface (8). Thermodynamic calculations (9) predict that, for representative fuel impurity levels and gas turbine conditions, the predominant equilibrium reaction will be



Increasing fuel sulfur levels (i.e., SO_3 partial pressures) therefore will tend to increase the V_2O_5 activity in the surface salt deposit.

These several effects were well illustrated in experiments (7) studying the influence of SO_3 in the corrosion of 35 wgt-% chromium CoCrAlY coated with Na_2SO_4 , V_2O_5 , or NaVO_3 . As seen in Fig. 3, the $\text{NaVO}_3/\text{SO}_3$ samples exhibited

an abrupt rise in corrosion rate after about 16 hours, and which was then followed at about 24 hours, by an apparent cessation of corrosion, or "inhibition." This behavior was explained by metallurgical examination (cf. ref. 7 for details) of samples taken before (Figs. 4,5) and after (Fig. 6) the onset of "inhibition." Initial reaction of SO_3 with NaVO_3 produces a molten phase (the gray phase marked A in Fig. 5) rich in CoSO_4 and Na_2SO_4 which is essentially a CoSO_4 - Na_2SO_4 eutectic and from which, as the V_2O_5 activity in the melt increases, a cobalt vanadate phase is precipitated (white phase marked B in Fig. 5). Inhibition occurs when the amount of precipitated cobalt vanadate (B in Fig. 6) becomes sufficient to "seal off" the corrosion phase surface.

However, note that the outer cobalt vanadate layer in Fig. 6 has many cracks, and would almost certainly spall away in an engine gas stream. The phenomenon of outer vanadate layer formation and spallation has in fact been observed in both earlier (10) and more recent (11) research on vanadate corrosion. It is unlikely therefore that any meaningful inhibition by vanadate layers could be achieved in engine use.

A major distinction between sulfate and vanadate hot corrosion is the extended inner oxide layer that forms beneath molten vanadate-rich deposits (cf. Fig. 4, also refs. 10,11). No evidence of a liquid phase is discernible in this inner oxide, and Moller (10) argues that corrosion at the metal interface does not involve a liquid phase (such as the molten sulfates or sulfides postulated for sulfate corrosion), but proceeds by solid/gas transport, which is promoted by incorporation of trace vanadium in the oxide lattices. It may also be that, since the lowest oxidation state normally exhibited by vanadium is 2^+ , no equivalent of a "liquid sulfide" occurs in vanadic hot corrosion.

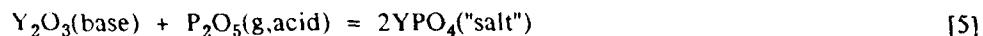
Several differences--the ability to form refractory vanadates, the unique inner oxide layer, the interaction between sulfur and vanadium species--thus distinguish vanadate or vanadate/sulfate hot corrosion from sulfate hot corrosion. Present metallic alloys and coatings optimized for molten sulfate resistance may not be satisfactory therefore for fuels with significant vanadium levels, and ultimately new metals may have to be designed to withstand simultaneous sulfur/vanadium attack.

FUEL IMPURITY CORROSION OF CERAMICS

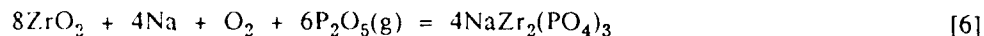
Advanced engine ceramics include coatings such as heat-insulating thermal barrier coatings (TBC's) of stabilized zirconia to increase engine thermal efficiency, and integral components such as gas turbine vanes, turbocharger rotors, or cylinder liners which are likely to be fabricated from silicon carbide or nitride. Note that all ceramics intended for oxygen-rich engine environments are either oxides, or form protective surface oxides (e.g., SiC and Si_3N_4). Oxide acid-base reactions are therefore likely to be predominant in their corrosion processes, even more than for metals. Accordingly, the following discussions, which review briefly ceramic corrosion results with the fuel contaminants phosphorus, lead, sulfur, and vanadium, are couched largely in acid-base terminology, but other factors such as coordination reactions, diffusion kinetics, and ceramic physical structure are also undoubtedly important.

Phosphate Corrosion of Stabilized Zirconia

Yttria-stabilized zirconia has been shown (12) to be attacked and destabilized by phosphorus impurities in fuel. The reaction can be written in acid-base terms as



Zirconia was also reported to react when sodium was present by a reaction written by the authors (12) as



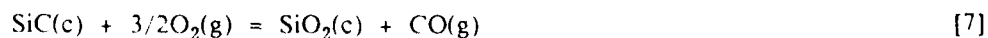
This finding is significant since efforts to develop corrosion-resistant stabilized zirconia (see below) have focused on improving the stabilizer, with zirconia itself being considered nonreactive.

Lead Corrosion of Zirconia Thermal Barrier Coatings

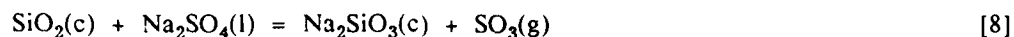
Yttria-stabilized zirconia thermal barrier coatings have been tested in $\text{PbSO}_4\text{-Na}_2\text{SO}_4$ molten salts with no discernible destabilization or reaction of the ceramic (13). However, lead appeared to accelerate TBC corrosion by reaction with chromium from the NiCrAlY bond coat, with PbCrO_4 being formed (i.e., where PbO is acting as a base).

Sodium Sulfate Corrosion of SiC and Si_3N_4

This topic has been studied by several laboratories, but perhaps most recently at NASA (14,15). The critical reactions were identified as



followed by, or concurrently with



The last reaction is an acid-base displacement with one acid, SiO_2 , displacing a second, SO_3 . Reaction [8] is thermodynamically unfavorable, but proceeds because SO_3 is removed by the flowing gas. Sulfur trioxide in the reaction gas inhibits reaction [8], and SiC which has no excess carbon is virtually inert to $\text{Na}_2\text{SO}_4/\text{SO}_3$. However, excess carbon often occurs in silicon carbides, and its oxidation leads to a complex, thermodynamically highly favored reaction which causes dissolution of the protective SiO_2 on SiC even in gases with appreciable SO_3 .

Molten Na_2SO_4 reacts with Si_3N_4 forming Na_2SiO_3 and generating N_2 (by reactions similar to [7] and [8]), but corrosion is slower than with SiC , possibly because N_2 is transported more slowly than SO_3 through the Na_2SO_4 - Na_2SiO_3 surface film. Even limited corrosion resulted in significant loss of ceramic strength, however, and question thus remains as to the viability of silicon-based ceramic components in engines burning high Na/S fuel.

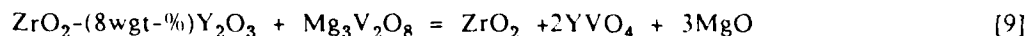
Sulfate/ SO_3 Corrosion of Stabilized Zirconia

Although little studied, concurrent attack by Na_2SO_4 and SO_3 has been shown to destabilize both magnesia (16) and yttria (17) stabilized zirconia, with formation of MgSO_4 - Na_2SO_4 and $\text{Y}_2(\text{SO}_4)_3$ - Na_2SO_4 mixed sulfates, respectively. Subsequent work (18) confirmed the reactivity of Y_2O_3 with $\text{Na}_2\text{SO}_4/\text{SO}_3$, while demonstrating that ZrO_2 itself was resistant to reaction with $\text{Na}_2\text{SO}_4/\text{SO}_3$.

Vanadate Corrosion of Stabilized Zirconia

Numerous laboratories have investigated molten vanadate corrosion of yttria-stabilized zirconia and reported destabilization and ceramic degradation caused by "leaching out" of the yttria, with the product YVO_4 usually being identified on the ceramic surface. Insight into the reaction mechanism has been lacking, however, except in a few instances. In one study (19), the corrosion of ZrO_2 -(8wgt-%) Y_2O_3 by $NaVO_3$ - Na_2SO_4 melts under equilibrated SO_2 - SO_3 - O_2 gas mixtures was shown to increase directly with SO_3 partial pressure, and with the square of $NaVO_3$ concentration. This behavior was explained by noting that these dependences were the same as would increase V_2O_5 activity in the melt (cf. reaction [4]), which in turn would cause YVO_4 formation (reaction [2]) and ceramic depletion/corrosion.

The importance of acid-base reaction is manifested also in the finding (16) that $Mg_3V_2O_8$ ($3MgO \cdot V_2O_5$) readily causes zirconia destabilization by



which is an acid-base displacement with Y_2O_3 displacing MgO in reaction with V_2O_5 . The implications of reaction [9] may be supported by diesel service experience (20), where MgO -stabilized ZrO_2 has been found superior to Y_2O_3 -stabilized ZrO_2 against vanadic hot corrosion, but the reverse to be true, interestingly, for sulfate hot corrosion.

The concept of acid-base reaction in ceramic corrosion has been investigated (21) also in terms of a "reaction matrix" (Fig. 7) between the different vanadium

compounds and various ceramic oxides. The data in Fig. 7 reflect classic acid-base behavior where acids react with bases, and vice versa, but no reaction occurs between compounds of comparable acid-base nature. Note that NaVO_3 acts as an acid with basic Y_2O_3 but as a base with acidic GeO_2 or Ta_2O_5 .

Fig. 7 indicates also that ZrO_2 , presumably because of its acid-base character, is essentially nonreactive with vanadium compounds (the V_2O_5 reaction is very slow), and that a highly vanadate-resistant stabilized zirconia might be possible, if an effective stabilizer having a more acidic nature than Y_2O_3 (or MgO and CaO) could be found.

One such potential stabilizer is CeO_2 (which in fact has been patented as a sulfate/vanadate resistant stabilizer (22)), but in tests (23) with NaVO_3 , CeO_2 -stabilized ZrO_2 was destabilized to virtually the same extent as Y_2O_3 -stabilized ZrO_2 , even though pure CeO_2 and ZrO_2 had been found (Fig. 7) not to react with NaVO_3 . This paradox, which brings doubt on the possibility of ceramic design by oxide acid-base theory, has yet to be resolved. Ceria has (23) a physical solubility in NaVO_3 of about 0.1 mol-% at 700°C to 1 mol-% at 1000°C , but it is not certain how much this contributes to the destabilization process.

Perhaps more relevant was the showing (23) that reaction of V_2O_5 with ZrO_2 -(20wt-%) CeO_2 produced a CeVO_4 surface phase (Fig. 8a,b), whereas reaction of NaVO_3 under the same conditions yielded surface crystals of segregated CeO_2 (Fig. 9a,b). This may indicate a flaw in the approach taken in Fig. 7; i.e., the assumption that the acid-base reaction tendencies of pure oxides are unchanged when the oxide is incorporated as a minority component in a ceramic structure. Experience with glass and solid state catalysts suggests that the relative acid-base strengths of oxides may be modified when they are introduced into a foreign

oxide matrix. It is conceivable therefore that the acid-base nature of CeO_2 is changed under the influence of a ZrO_2 matrix so that CeO_2 in ZrO_2 gives reaction with NaVO_3 , although pure CeO_2 alone does not.

One promising approach for studying interactions between stabilizing oxides and the zirconia oxide lattice (which is possibly the key for the development of corrosion-resistant zirconia) is the "optical basicity" technique of Duffy (2). This technique measures the shift in energy of electronic transitions of "probe ions" (e.g., Pb^{2+} , Fig. 10) as these energies are affected by electron charge donation (i.e., the factor determining Lewis acid-base nature) from oxygen atoms in the oxide matrix lattice, with the relative "basicity" of the glass or other oxide material being calculated from the energy shift measurements. Application to zirconia is hindered because ZrO_2 has a strong adsorption peak at $43,500\text{ cm}^{-1}$, but peak deconvolution techniques may be a means to surmount this difficulty.

CLOSURE

No discussion has been offered concerning fuel contaminant corrosion of the fiber-reinforced composites, specially processed metals or "exotic" ceramics that were included under the definition of advanced materials in the Introduction.

This is mainly because the open literature contains very little on the topic. On the other hand, one would hope that corrosion of such materials could often be treated not as "new", but simply as combinations of known corrosion systems on which knowledge, as described above, is available.

As for new directions in research, one need (obviously dear to the author) is to quantify how much ceramic corrosion is controlled by oxide acid-base reaction -- championed strongly here -- and how much by other atomic interactions, diffusion processes, or alternative factors. For example, solubilities

of the type provided by Rapp (Fig. 1) for oxides in molten Na_2SO_4 , but for the high temperature $\text{Na}_2\text{O-V}_2\text{O}_5$ and $\text{Na}_2\text{O-P}_2\text{O}_5$ systems, could prove informative. It may be found that as the acidic components become more capable of network formation (i.e., with P_2O_5), the acid-base reactivity trends may change so that oxides resistant to one acidic salt system (ZrO_2 to $\text{Na}_2\text{SO}_4/\text{SO}_3$ or NaVO_3) may not be resistant to a second system (ZrO_2 to $\text{Na}_2\text{O-P}_2\text{O}_5$).

Finally, physical processing should not be neglected as a means for improving corrosion performance of ceramics or other advanced materials. Processing that improves chemical homogeneity, minimizes easy diffusion paths, reduces reactive impurity content, or develops beneficial phase structure may substantially increase corrosion resistance even of materials containing known (e.g., Y_2O_3) reactive components.

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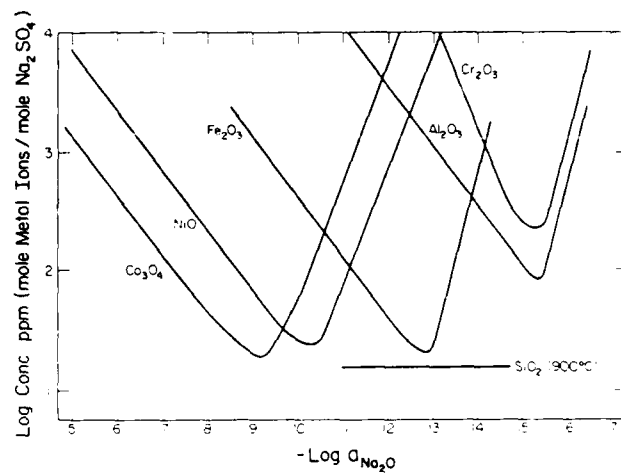


Fig. 1—Oxide Solubilities in fused Na_2SO_4 at 1200°K and 1 atm O_2 . (Taken from Ref. 6; used with permission.)

SODIUM VANADATE COMPOUNDS

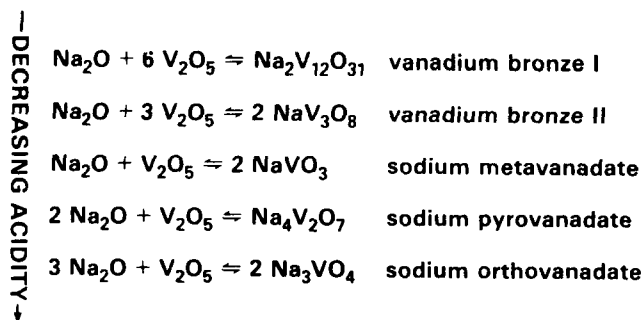


Fig. 2 —Vanadic compounds in $\text{Na}_2\text{O}-\text{V}_2\text{O}_5$ system. (Taken from Ref. 18; used with permission.)

CORROSION OF CoCrAlY AT 700°C BY PURE COMPOUNDS UNDER SO_3

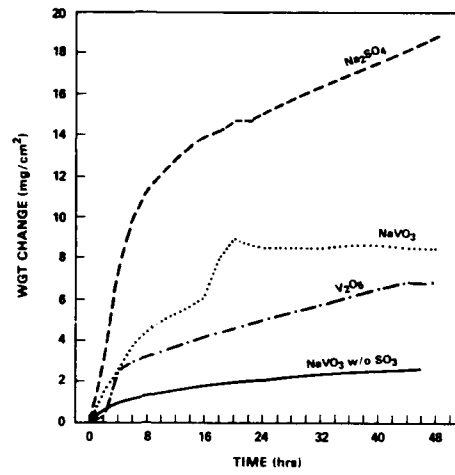


Fig. 3—Corrosion of CoCrAlY by various compounds under 13 Pa SO_3 in air at 700°C; ---curve is for NaVO_3 . (Taken from Ref. 7; used with permission.)

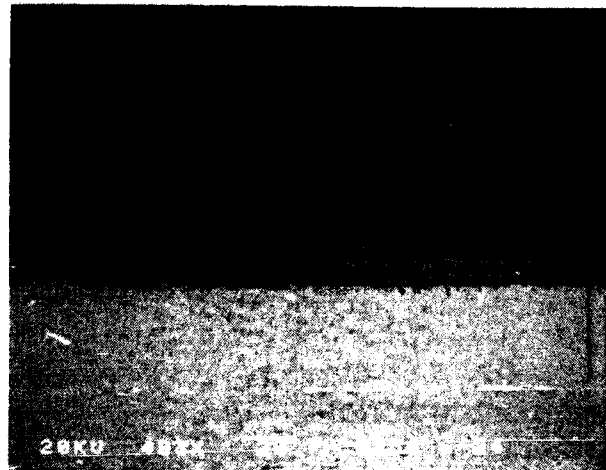


Fig. 4—CoCrAlY corroded 14.5 h at 700°C by $\text{NaVO}_3/\text{SO}_3$ (13 Pa). Note extensive oxide layer under molten vanadate phase.

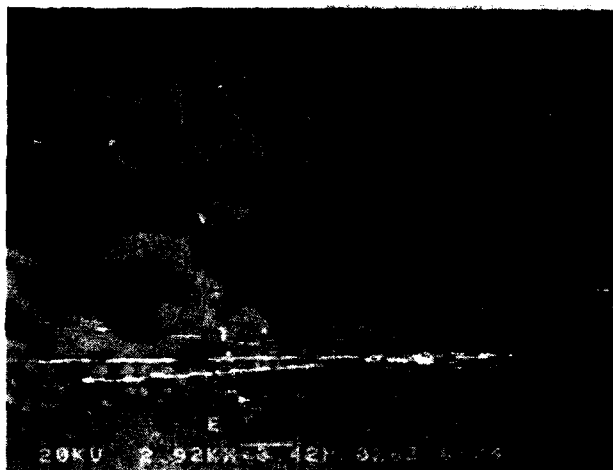
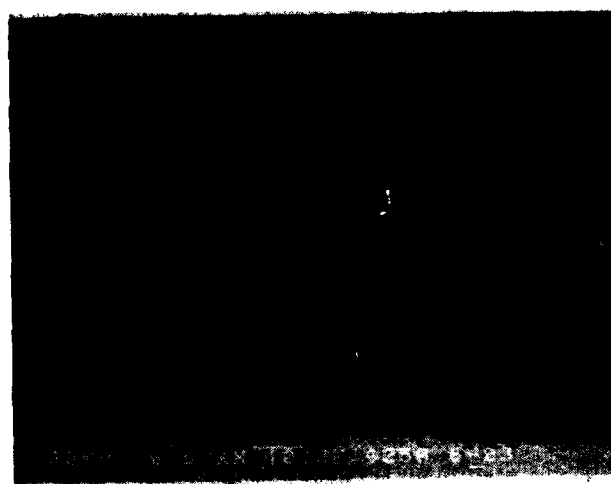


Fig. 5 —Higher magnification of Fig. 4.
(Taken from Ref. 7; used with permission.)

Fig. 6 —CoCrAlY corroded 48 h at 700°C by
NaVO₃/SO₃ (13 Pa). (Taken from Ref. 7; used
with permission.)



VANADIUM-CERAMIC OXIDE REACTIONS

	—INCREASING ACIDITY→		
	<u>Na₃VO₄</u>	<u>NaVO₃</u>	<u>V₂O₅</u>
↑	<u>Y₂O₃</u>	NR	YVO ₄
↑	<u>CeO₂</u>	NR	CeVO ₄
↑	<u>ZrO₂</u>	NR	ZrV ₂ O ₇ (BUT SLOWLY)
↑	<u>GeO₂</u>	Na ₄ Ge ₃ O ₂₀	Na ₄ Ge ₃ O ₂₀ ^(*)
↑	<u>Ta₂O₅</u>	NR	NR
↑		NaTaO ₃	Na ₂ Ta ₄ O ₁₁
↑			α-TaVO ₅
NR = NO REACTION			
(*) AS PPT FROM H ₂ O SOL'N			

Fig. 7—Reaction behavior of ceramic oxides
and vanadium compounds. (Taken from Ref.
21; used with permission.)



Fig. 8a — CeVO_4 crystallites produced by V_2O_5 on ZrO_2 -(20wt-%) CeO_2 . (Taken from Ref. 23; used with permission.)

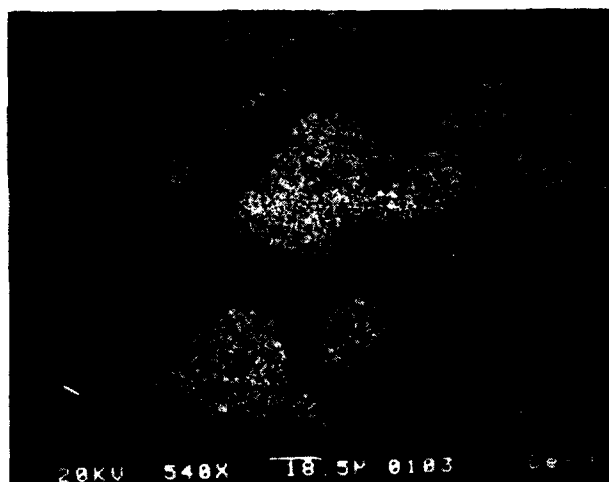


Fig. 8b —Ce-V Xray map of Fig. 8a. (Taken from Ref. 23; used with permission.)

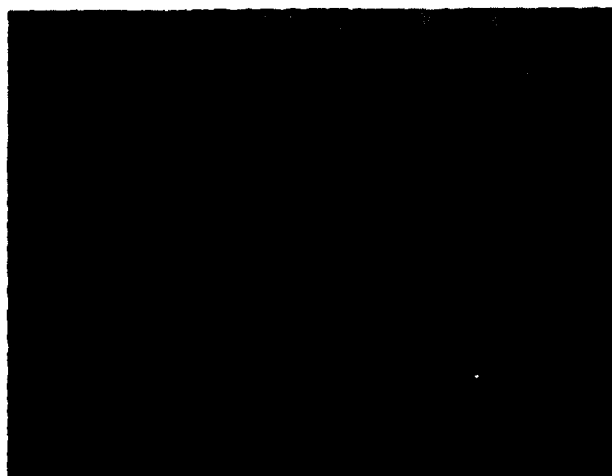


Fig. 9a and b.—Micrograph and Xray map of CeO_2 crystals produced by NaVO_3 on ZrO_2 -(20wt-%) CeO_2 . (Taken from Ref. 23; used by permission.)

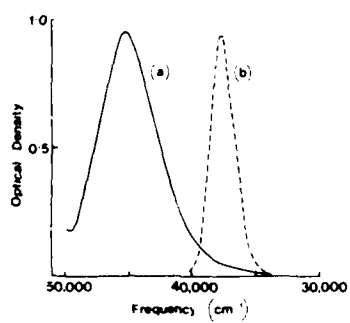


Fig. 10 —Absorption spectrum of Pb^{2+} in (a) sodium borate glass vs. (b) in 11 M HCl. (From Ref. 2; used by permission.)