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Some Aspects of the Hot Corrosion of Thermal Barrier Coatings

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This paper reviews the hot corrosion of zirconia-based thermal barrier coatings for engine applications. Emphasis is placed on understanding the chemical reactions, and such other mechanisms as can be identified, that cause corrosive degradation of the thermal barrier coating. The various approaches taken to improve the hot corrosion resistance of thermal barrier coatings are also briefly described and critiqued.

Keywords hot corrosion, molten salts, oxide acid-base reactions, thermal barrier coatings, zirconia phase stability

1. Introduction

BECAUSE OF their promise of improved engine efficiency and component life, thermal barrier coatings (TBCs) may be widely used in the future in industrial gas turbine or diesel engines burning low quality fuel or operating in corrosive environments. Thermal barrier coatings also are envisioned for military land or sea engines, which must be capable of surviving low-quality fuel and corrosive environments in wartime emergency. Therefore, to better understand, and to predict where possible, the potential effects of hot corrosion on TBCs is essential.

Most present-day engine TBCs are of the Y_2O_3(8 wt%)-stabilized ZrO_2 type. This material has been developed over many years and is currently thought to give the best TBC performance, especially in aviation gas turbines. Yttria-stabilized zirconia (YSZ) TBCs are normally applied by either atmospheric plasma spraying (APS) or electron beam/physical vapor deposition (EB-PVD) over bond coats that are usually MCrAlYs (where M = Ni, Co or Ni,Co), but may also be aluminides or various combinations. Schematic representations of APS and EB-PVD TBCs are shown in Fig. 1.

The details of TBC production by APS have been described by Miller (Ref 1), and those of TBC production by EB-PVD by Strangman (Ref 2). In APS, the zirconia layer is built up of "splatted down" molten droplets and contains a certain amount of porosity. This porosity is highly critical in determining the thermal cycle life of APS TBCs (Ref 1). In contrast, the EB-PVD zirconia layer consists of columnar particles that are "strain tolerant" and therefore thought to give increased thermal cycle life. Studies indicate that whereas APS coatings generally fail in the zirconia phase just at the bond coat/zirconia layer interface, perhaps because of strains introduced by oxidation of the bond coat (Ref 3), EB-PVD coatings fail within the bond coat oxide that is thermally grown on the bond coat during service life (Ref 4).

As recounted by Miller (Ref 1), many factors are crucial in obtaining satisfactory Y_2O_3-ZrO_2 TBC performance. These include the APS powder (Ref 5) and EB-PVD ingot themselves, the exact operating parameters used in the coating process, the composition and structure of the bond coat, and the physical and crystal structure of the zirconia layer. The achievement and maintenance of the so-called "nontransformable" tetragonal T′ phase structure, as first identified by Scott (Ref 6), appears particularly important. If ZrO_2 containing about 8 wt% (4.5 mol%) Y_2O_3 is heated into the cubic or molten phase regions of the Y_2O_3-ZrO_2 phase diagram (Fig. 2) and then quenched rapidly (as in APS or EB-PVD processing), the tetragonal T′ phase is produced (Ref 7, 8).

Evidence suggests that this phase is the major reason for the superior TBC performance of Y_2O_3(8 wt%)-ZrO_2, both in that it has a microcracked structure that may alleviate thermal stress (Ref 1), and in that it avoids the catastrophic (because it involves a 4 to 5% volume change) transformation between the tetragonal T phase and monoclinic phase that normally occurs with thermal cycling of zirconia. However, the T′ phase is metastable, and it undergoes phase separation into the low-Y_2O_3-content "transformable" tetragonal T phase and high-Y_2O_3-content cubic phase if isothermally aged at 1200 °C and above (Ref 7, 8). The resultant tetragonal T phase transforms as normal to the mono-

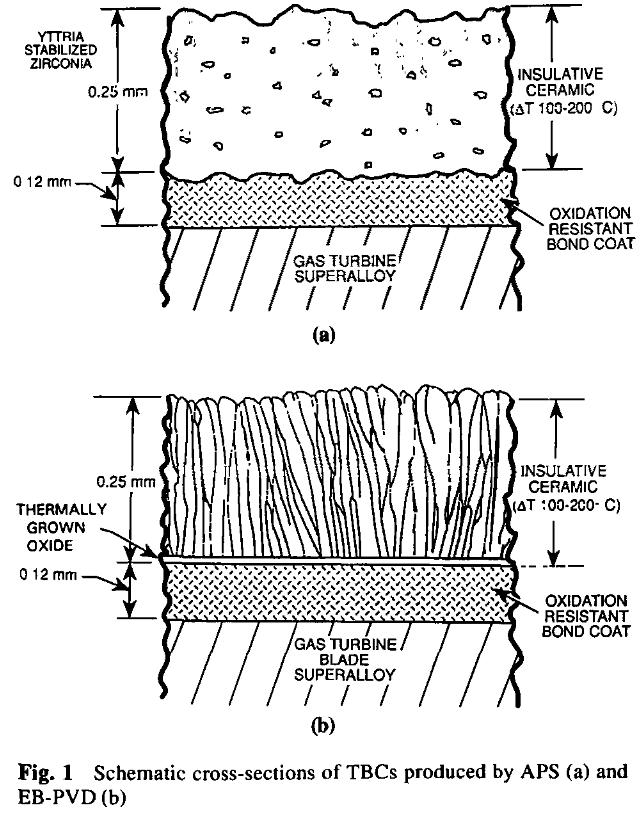

Fig. 1 Schematic cross-sections of TBCs produced by APS (a) and EB-PVD (b)

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clinic phase at low temperature, which promotes physical disintegration of the coating.

The phase transformations of the Y_2O_3-ZrO_2 system, especially cubic (F) → metastable tetragonal (T′) and tetragonal (T) → monoclinic (M), are of great interest in ceramic science and have been reviewed and compared by Heuer et al. (Ref 9). Recently, Sheu et al. (Ref 10) studied the F → T′ transformation for the ZrO_2-$MO_{1.5}$ systems where M = Sc, In, Y, and rare earths (R). They concluded, among other points, that the T′ and T phases are fundamentally the same tetragonal polymorph and differ only in their range of composition.

Other important papers concerning the tetragonal T′ phase are by Noma et al. (Ref 11) who show that apparent stability of the T′ phase up to 1700 °C can be obtained by certain processing, and by Virkar and Matsumoto (Ref 12), who propose that the T′ phase is toughened by a ferroelastic domain switching mechanism as opposed to T → M transformation toughening for the tetragonal T phase. Of interest to the TBC coating field are the results of Taylor et al. (Ref 13), which indicate that CeO_2(25 wt%)-ZrO_2 retains a tetragonal structure even after 100 h at 1400 °C and that CeO_2(25 wt%)-ZrO_2 might therefore be preferable to Y_2O_3(8 wt%)-ZrO_2 for ultrahigh-temperature TBC applications.

2. Modes of Hot Corrosion by Molten Deposits

Reactions with molten deposits would be intuitively expected to affect these critical phase transformations and thereby the performance of zirconia TBCs. However, this is difficult to demonstrate explicitly, since quantitative x-ray analysis for the various ZrO_2 phases is complex (Ref 8, 14), and even more so in the presence of comixed salt phases. Little evidence, therefore, can be found in the literature (except in the limited context discussed below) to show the effect of molten salts in driving the various zirconia transformations.

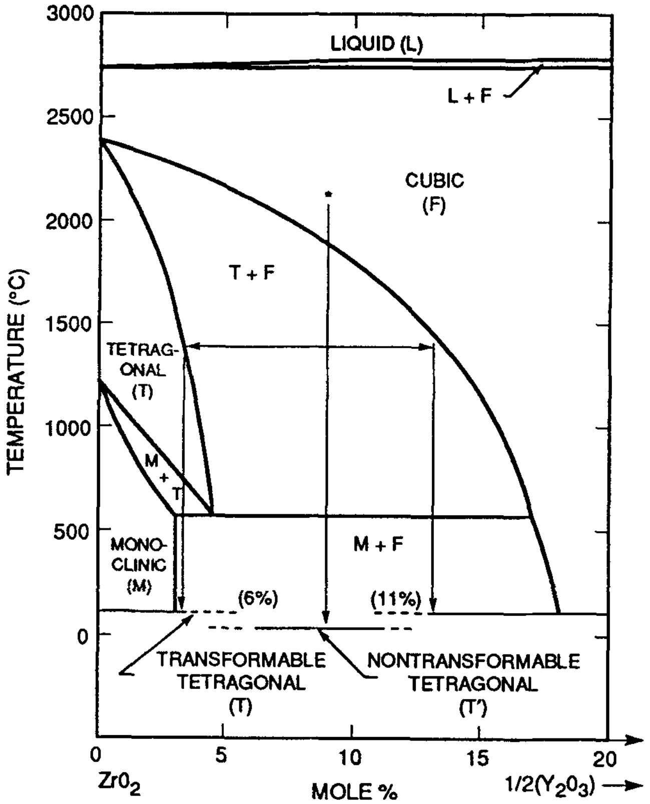

Fig. 2 Phase diagram of the Y_2O_3-ZrO_2 system illustrating phase reactions involving the tetragonal (T′) phase. Source: Ref 8

Hot corrosion of TBCs by molten deposits can be categorized into at least four different modes: attack by chemical reaction, by "mineralization," by corrosion of the bond coat, or by physical damage by molten phases penetrating into the TBC intergranular voids.

2.1 *Chemical Reaction*

Attack by chemical reaction is characterized by the presence of an identifiable reaction product and usually by the ability to postulate a specific reaction. The laws of stoichiometry and thermodynamics apply; therefore, the conditions for chemical reaction should be predictable, provided that the necessary thermodynamic and solution chemistry data are available.

The need for understanding the solution chemistry is illustrated in the well-known hot corrosion of Y_2O_3-stabilized ZrO_2 by V_2O_5 (see section 3). Since Y_2O_3(8 wt%)-ZrO_2 contains 4.5 mol% Y_2O_3, the Y_2O_3 activity, assuming ideal solid-solution behavior in ZrO_2, would be 0.045. However, activity coefficients of about 0.1 and 0.01 have been measured for Y_2O_3 and Sc_2O_3, respectively, in 5 mol% solid solution in ZrO_2 at 2300 to 2500 °C (Ref 15, 16). These activity coefficients should be even smaller at lower temperatures (since systems tend to move *away* from ideal behavior as the temperature decreases), with the Y_2O_3 activity in Y_2O_3(8 wt%)-ZrO_2 at 1000 °C therefore being perhaps on the order of 4.5×10^{-4} or below.

Nonideal behavior is also observed for V_2O_5 itself in vanadate-sulfate melts, with an activity coefficient of approximately 0.01 being found for V_2O_5 in $NaVO_3$ melts equilibrated under low partial pressures of SO_3 at 800 °C (Ref 17). Thus, the assumption of ideal solution behavior will cause serious error in thermodynamic calculations of V_2O_5 reaction with Y_2O_3(8 wt%)-ZrO_2. Another factor to consider is that chemical reaction between ceramic oxides and corrosive melts, even when thermodynamically possible, may be significantly slowed by intrinsic reaction kinetics, slow diffusion through condensed phases, or the formation of a product "barrier" layer.

2.2 *Mineralization*

Mineralization is a type of phase reaction involving a "nonreactive" liquid that tends to move a stressed or nonequilibrium phase toward equilibrium. The mechanism is generally undefined, although it may entail limited dissolution and precipitation. Mineralization has been used extensively in obtaining phase equilibrium in silica systems and in certain zirconia systems (Ref 18). An example where molten $NaVO_3$ apparently has acted to mineralize CeO_2(20 wt%)-ZrO_2 is cited in section 4.4.

2.3 *Bond Coat Corrosion*

Although this paper is concerned with the hot corrosion of zirconia TBCs, the zirconia layer may actually be more resistant to hot corrosion, especially sulfate-induced hot corrosion, than the MCrAlY or aluminide bond coat (Ref 19, 20). In his review of TBCs for electric utility gas turbines, Miller (Ref 20) cites three reports where the thin residue of zirconia left after spalling of the zirconia layer was found to protect the underlying bond coat from hot corrosion. It is conceivable that molten corrodents could, under some conditions, penetrate the "inert" zirconia layer to corrode the bond coat and cause the TBC to fail. Specific evidence of hot corrosion of the bond coat under an intact ZrO_2 layer is hard to verify, however. Extensive hot corrosion of the bond coat is usually found only at sites of spalled ZrO_2, as extensions under the ZrO_2 at the edge of a spall site, or under clearly detached ZrO_2, which makes it difficult to confirm whether the corrosion in fact occurred before or after the spalling of the zirconia.

The penetration of corrosive *gases* through the zirconia layer must also be considered a possibility. In metallic hot corrosion, vaporous NaCl has been found to cause the growth of a less protective and thicker Al_2O_3 film on CoCrAlY (Ref 21), and the passage of vaporous NaCl (or HCl or Cl_2) through the ZrO_2 layer might, in a similar manner, result in an accelerated growth of Al_2O_3 on the bond coat surface, which would in turn promote spalling of the ZrO_2 layer.

2.4 *Physical Damage by Molten Salt Penetration*

Physical damage has been a continuing concern for TBCs used in deposit-producing high-temperature environments, and such damage has gained new attention because of the possibility of melt penetration between the columnar grains of TBC coatings produced by EB-PVD. Miller (Ref 20) discusses the conditions under which molten deposit penetration into the zirconia layer of TBCs may occur. Since vanadate-sulfate melts contract upon solidification, compressive stresses should not develop as molten deposits "freeze" within the TBC porosity upon cooling. Nonetheless, the presence of melt phases within the voids or columnar grain boundaries of the TBC zirconia is likely to reduce the tolerance of the TBC to thermal and physical stresses, even if chemical reaction or extensive sintering does not occur.

3. Past Experience in TBC Hot Corrosion

The majority of research on the hot corrosion of TBCs occurred during the fuel crisis of the 1970s and, at least in the United States, was sponsored primarily by the U.S. Department of Energy (DOE). This work has been reported in DOE conferences of 1979, 1982, and 1987. Other TBC hot corrosion studies relating to electric utility gas turbines have been summarized by Miller (Ref 20). One of the first workers in the field of TBC hot corrosion was Kvernes, who has published numerous papers, including a 1986 review that describes many of his results as well as other TBC corrosion studies in Europe (Ref 22). The present paper draws heavily from these sources.

Experience to date indicates that the principal corrosive fuel impurities capable of causing TBC hot corrosion are sodium, sulfur, vanadium, and possibly also lead and phosphorus. Molten silicates from ingested desert sands are now also considered a hot corrosion threat for TBCs at very high temperatures (Ref 23). During combustion, the fuel impurities are oxidized to form oxides that have strong acid or base properties and that undergo reactions such as:

$$Na_2O\,(\text{base}) + SO_3\,(\text{acid}) \leftrightarrow Na_2SO_4\,(\text{salt}) \qquad (\text{Eq } 1)$$

$$Na_2O\,(\text{base}) + V_2O_5\,(\text{acid}) \leftrightarrow 2NaVO_3\,(\text{salt}) \qquad (\text{Eq } 2)$$

Solid inorganic oxides also have innate Lewis acid-base natures, and by studying the high-temperature reactions of compounds such as Na_3VO_4 ($3Na_2O \cdot V_2O_5$), $NaVO_3$ ($Na_2O \cdot V_2O_5$), and V_2O_5 itself with TBC (and other) oxides (Ref 24), the potential importance of acid-base interactions in the hot corrosion of TBCs can be demonstrated (Fig. 3). Note in Fig. 3 that acids react with bases, and vice versa, but that no reaction occurs between compounds of comparable acid-base strength. Note also that $NaVO_3$ acts as an acid toward basic Y_2O_3, but as a base toward acidic GeO_2 or Ta_2O_5.

The following review of TBC hot corrosion results is not exhaustive, but rather touches only on those works that serve to illustrate the general TBC hot corrosion experience. McKee et al. (Ref 25) examined the hot corrosion of APS Y_2O_3-ZrO_2 thermal barrier coatings by deposits typical of sodium, sulfur, lead, and vanadium fuel impurities, as well as in burner rig tests burning NaCl and sulfur-doped fuel. After 871 °C burner rig tests, Na_2SO_4 was found in the pores of the zirconia layer, but x-ray diffraction showed no destabilization of the YSZ crystal structure. However, sulfide formation was detected at the substrate IN-738 superalloy/bond coat interface, indicating penetration of the molten sulfate (or possibly a gaseous S_2 phase) through both the zirconia layer and APS NiCrAlY bond coat. Crucible tests with molten vanadates resulted in YVO_4 formation and in cracking and spalling of the YSZ zirconia. Molten $PbSO_4$-Na_2SO_4 in crucible tests gave no discernible destabilization or reaction of the YSZ ceramic, but there was corrosion of the NiCrAlY bond coat, with $PbCrO_4$ being formed (presumably by reaction of PbO [base] with Cr_2O_3 [acid]).

INCREASING ACIDITY →

INCREASING ACIDITY ↓

	Na_3VO_4	$NaVO_3$	V_2O_5
Y_2O_3	NR	YVO_4	YVO_4
CeO_2	NR	NR	$CeVO_4$
ZrO_2	NR	NR	ZrV_2O_7 (BUT SLOWLY)
GeO_2	$Na_4Ge_9O_{20}$	$Na_4Ge_9O_{20}$(*)	NR
Ta_2O_5	$NaTaO_3$	$Na_2Ta_4O_{11}$	α-$TaVO_5$

NR = NO REACTION

(*) AS PPT FROM H_2O SOL'N

Fig. 3 Reaction behavior of ceramic oxides with vanadium oxide compounds of varying acidity. Source: Ref 24

In 800 °C burner rig tests using GT No. 2 fuel doped with various levels of sodium, vanadium, phosphorus, calcium, iron, magnesium, and sulfur, Bratton et al. (Ref 26, 27) found that magnesia-stabilized zirconia (MSZ) is destabilized by:

$$ZrO_2(MgO) + SO_3\,(g) \rightarrow ZrO_2\,(\text{monoclinic}) + MgSO_4 \qquad (\text{Eq } 3)$$

For fuels containing no magnesium, destabilization of MSZ occurs also by reactions of the type:

$$ZrO_2(MgO) + V_2O_5\,(l) \rightarrow ZrO_2\,(\text{monoclinic}) + Mg_3V_2O_8 \qquad (\text{Eq } 4)$$

When both V_2O_5 and SO_3 are present, they compete for reaction with the MgO stabilizer, much as the case when MgO inhibitors are used with vanadium and sulfur-containing fuels (Ref 28). Destabilization may occur by either $MgSO_4$ or $Mg_3V_2O_8$ formation, depending on the specific activities of SO_3 and V_2O_5 in the corrodent melt.

For Y_2O_3-stabilized ZrO_2 TBCs, Bratton et al. (Ref 26, 27) concluded that, when both magnesium and vanadium are present in the fuel and react to form $Mg_3V_2O_8$, the destabilization reaction is:

$$ZrO_2(Y_2O_3) + Mg_3V_2O_8 \rightarrow ZrO_2\,(\text{monoclinic}) + 2\,YVO_4 + 3\,MgO \qquad (\text{Eq } 5)$$

In the absence of magnesium in the fuel, the destabilization reaction as determined by Kvernes et al. (Ref 29), Hamilton and Nagelberg (Ref 30), and others is simply:

$$ZrO_2(Y_2O_3) + V_2O_5 \rightarrow ZrO_2\,(\text{monoclinic}) + 2YVO_4 \qquad (\text{Eq } 6)$$

Details of the specific course of reaction of V_2O_5 with YSZ, as well as the diffusion behavior of vanadium and yttrium within the YSZ matrix, are given by Hertl (Ref 31). The crystallographic aspects of the reaction of V_2O_5 with Y_2O_3-stabilized ZrO_2 have also been examined by transmission electron microscopy by Susnitzky et al. (Ref 32).

Note that reactions shown in Eq 5 and 6 indicate Y_2O_3 to be a stronger base than MgO; that is, the stronger base, Y_2O_3, displaces the weaker base, MgO, from reaction with acidic V_2O_5 by:

$$Mg_3V_2O_8 + Y_2O_3 \rightarrow 2YVO_4 + 3MgO \qquad (\text{Eq } 7)$$

If the fuel contains no vanadium but has high sulfur, YSZ may be destabilized by the reaction of Y_2O_3 with SO_3 in the presence of Na_2SO_4, as shown by Barkalow and Pettit (Ref 33), according to:

$$ZrO_2(Y_2O_3) + 3\,SO_3(+\,Na_2SO_4) \rightarrow Y_2(SO_4)_3\ (\text{in } Na_2SO_4 \text{ solution}) \qquad (\text{Eq } 8)$$

The reaction occurred more readily at low temperature (704 °C) than at high temperature (982 °C) and required SO_3 partial pressures on the order of 10^{-4} atm at 704 °C and 10^{-3} atm at 982 °C for significant reaction to take place. In general, YSZ TBCs may thus tend to resist sulfur degradation but be susceptible to vanadium degradation. On the other hand, MSZ is more susceptible to sulfur degradation (Ref 26), but could possibly be superior to YSZ in resistance to attack by V_2O_5, as indicated by the reactions shown in Eq 5 to 7.

No chemical reaction of the ZrO_2 matrix itself with V_2O_5 or SO_3-Na_2SO_4 is normally detected in the hot corrosion of TBCs. However, Singhal and Bratton (Ref 26) found that reaction of ZrO_2 may occur when phosphorus is present as a fuel contaminant. (Petroleum fuels tend to contain little phosphorus, but phosphorus may be found in alternative fuels such as those derived by coal liquefaction.) Destabilization of YSZ by P_2O_5 occurs by the reaction:

$$ZrO_2(Y_2O_3) + P_2O_5 \rightarrow ZrO_2\,(\text{monoclinic}) + 2YPO_4 \qquad (\text{Eq } 9)$$

When sodium is present, Singhal and Bratton report that there can also be reaction of the ZrO_2 by:

$$8ZrO_2 + 4Na + O_2 + 6P_2O_5\,(g) \rightarrow 4NaZr_2(PO_4)_3 \qquad (\text{Eq } 10)$$

while Jones (Ref 34) has shown that ZrO_2 reacts readily with P_2O_5 according to:

$$ZrO_2 + P_2O_5\,(l) \rightarrow ZrP_2O_7 \qquad (\text{Eq } 11)$$

Silica in the form of silicates derived from desert sand is a threat to aircraft engines using TBCs at very high temperatures (>1200 °C). Stott et al. (Ref 23) have studied the attack of various desert sand melts and silicate glasses at 1400 to 1600 °C on specimens of both APS and EB-PVD Y_2O_3(8 wt%)-ZrO_2. Two mechanisms of attack were identified, depending primarily on the amount of CaO in the melt. While both ZrO_2 and Y_2O_3 were extracted from the YSZ by low-CaO melts, proportionately more Y_2O_3 was extracted, and the YSZ became partially monoclinic because of Y_2O_3 depletion. In the high-CaO melts, less Y_2O_3 was extracted, and there was diffusion of CaO into the ZrO_2 matrix, with the net effect being that the YSZ tended to remain in the tetragonal crystal structure. Substantial damage to the YSZ ceramic resulted in each case, however. The deleterious effect of silica as a materials impurity on the thermal cycle life of Y_2O_3(7 wt%)-ZrO_2 TBCs has also been recently established by Miller et al. (Ref 35).

Finally, although not directly relevant to TBC hot corrosion, tests by Mitamura et al. (Ref 36) of ZrO_2 partially stabilized by 3 mol% (5.4 wt%) Y_2O_3 in alkaline halide melts at 850 to 1050 °C are of interest. No T → M transformation was observed in Na_2CO_3, NaCl + KCl, Na_2SO_4 + NaCl, or K_2SO_4; however, when Na_2SiF_6 was added, there was extensive and rapid T → M transformation. No yttria reaction products were detected in the salt, and electron microprobe analysis indicated that Y_2O_3 remained in the ZrO_2 ceramic; however, fluorine, silicon, and sodium had diffused into the ceramic, where they may have been the cause of the rapid T → M transformation. In contrast, tests with molten PbF_2 at 900 °C resulted in very vigorous corrosion of the Y_2O_3(3 mol%)-ZrO_2, but no T → M transformation. The authors concluded that the tetragonal phase remained stable because of a strong (physical) restriction on the T-phase particles by the lead element that had permeated into the sintered zirconia body. These "fluoride effects" are a useful reminder that there may yet be important interactions between hot corrosion melts and stabilized zirconia TBCs that have not been identified.

4. Approaches to Improvement of TBC Hot Corrosion Resistance

Generally speaking, four approaches have been taken toward developing TBCs that tolerate hot corrosion:

- Use a different material than zirconia.
- Change the Y_2O_3 content.
- Provide "laser glazing" or seal coats to prevent salt penetration into the YSZ.
- Seek new corrosion-resistant stabilizers for ZrO_2, since the stabilizing oxide has appeared to be the weak point in zirconia TBC corrosion performance.

4.1 *Different TBC Materials*

In the past, several different materials—such as $CaTiO_3$, $ZrSiO_4$, $ZrTiO_4$, and Ca_2SiO_4—have been proposed for corrosion-resistant "thermal barrier" use. These materials have not come into widespread application. They do not offer the high thermal insulation of zirconia and commonly have a lower (less desirable) coefficient of thermal expansion (CTE). They may also have their own corrosion problems; for instance, Ca_2SiO_4 was found (Ref 26) to be susceptible to reaction with SO_3 in the burner rig gas by:

$$Ca_2SiO_4 + 2SO_3(g) \rightarrow 2CaSO_4 + SiO_2 \qquad \text{(Eq 12)}$$

Another proposal (Ref 37) has been to add Al_2O_3 and SiO_2 to Y_2O_3-ZrO_2 so as to, upon sintering, envelope the $ZrO_2(Y_2O_3)$ crystallites with zirconium and aluminum silicates, which then protect the YSZ crystallites from Y_2O_3 depletion during V_2O_5 hot corrosion. However, given the recent findings of Miller et al. (Ref 35) on the harmful effect of silica in YSZ coatings, one would expect that the thermal cycle life of such coatings would be reduced, at least in aircraft applications.

An alternative high-temperature thermal barrier candidate, $(Ca_{1-x}Mg_x)Zr_4(PO_4)_6$, has been more recently developed and is reported to have lower thermal conductivity than zirconia, as well as a CTE of near zero (Ref 38). It is not certain, however, whether this material would be suitable for TBC usage, or whether it has been tested for hot corrosion resistance. Taken in total, several decades of TBC development indicate that when all of the necessary properties for successful TBCs are considered, stabilized zirconia remains difficult to replace, especially for aircraft use.

4.2 *Higher Y_2O_3 Content*

Increasing the Y_2O_3 content of YSZ might be proposed as a means to improve hot corrosion resistance, either by providing "excess" Y_2O_3 to allow for a certain amount of Y_2O_3 depletion without TBC degradation, or by stabilizing the cubic (F) structure (Fig. 2) and avoiding the troublesome T → M transformation altogether. This idea was addressed by Miller (Ref 20) who, after reviewing the literature, points out that the thermomechanical performance of Y_2O_3(6 to 8 wt%)-ZrO_2 is so superior to that of higher Y_2O_3 compositions that the overall benefit (corrosion versus spalling) gained by increasing the Y_2O_3 content is likely to be minimal at best.

4.3 *Sealing the TBC Surface*

Over the years (and still today) efforts have been made to close the surface of zirconia TBCs by laser glazing or using various "seal coats" to prevent penetration of molten deposits into the zirconia voids. Miller (Ref 20) describes some of the early work in this area. None of these procedures has yet come into common use, perhaps because of the few applications of TBCs in engines or other applications where heavy surface deposits are developed. There is also the problem of reliably avoiding local penetrations or cracking of the seal coat under long-term, high-temperature conditions.

The question of salt penetration also needs to be further explored. Nagaraj et al. (Ref 39) note that, in addition to the Y_2O_3(8 wt%)-ZrO_2 not being destabilized, there was no penetration of salt into the TBC, or corrosion of the underlying bond coat, in burner rig tests of APS and EB-PVD yttria-stabilized zirconia TBCs at 704 °C (2 wt% S, 10 ppm sea salt) or 927 °C (0.4 wt% S, 5 ppm sea salt). Aircraft engine tests also showed no infiltration of salt through the TBC zirconia or bond coat corrosion, although Na_2SO_4 deposits were detected on the TBC surface, and aluminide coatings on the adjacent vanes were significantly hot corroded (Ref 40). On the other hand, Strangman and Schienle (Ref 19) have observed wicking of molten deposits into the intracolumnar porosity of EB-PVD thermal barrier coatings, but propose that the wicking may be minimized by densifying the outer EB-PVD surface by various means. It must be expected that TBC penetration will depend not only on the TBC porosity parameters but also, and perhaps primarily, on the composition and wetting properties of the specific deposit, with V_2O_5-containing melts known to be particularly wetting.

4.4 *Corrosion-Resistant Stabilizers*

Although ZrO_2 itself is resistant to reaction with either SO_3-Na_2SO_4 (Ref 41) or V_2O_5-containing melts (Ref 24), the commonly used CaO, MgO, or Y_2O_3 stabilizers for zirconia react readily with these corrodents, forming either the corresponding sulfate or vanadate. Therefore, corrosion-resistant stabilizers for ZrO_2 have been sought, with CeO_2, Sc_2O_3, and possibly In_2O_3 being the stabilizers that thus far have been proposed for improving TBC corrosion resistance.

4.4.1 Ceria

Ceria was patented as improving TBC hot corrosion performance in 1982 (Ref 42). Subsequent laboratory tests confirmed that CeO_2 (presumably because of its greater Lewis acidity) is more resistant to chemical reaction with SO_3-Na_2SO_4 (Ref 41) and sodium vanadates (Ref 24) than Y_2O_3. However, other laboratory tests (Ref 43) indicated that CeO_2(20 wt%)-ZrO_2 (CSZ) was as rapidly destabilized as Y_2O_3(8 wt%)-ZrO_2 by molten $NaVO_3$, even though pure ZrO_2 and CeO_2 separately did not react chemically with $NaVO_3$.

The product of destabilization was not $CeVO_4$, however, but rather monoclinic ZrO_2 with surface crystals of CeO_2 (containing some zirconium). These are the equilibrium phases for the ZrO_2-CeO_2 system, as determined by Tani et al. (Ref 44), at the 700 to 900 °C temperatures involved (Fig. 4). The destabilization of CSZ by pure molten $NaVO_3$ is therefore evidently a mineralization effect. In contrast, when CSZ is destabilized by V_2O_5 or $NaVO_3$-V_2O_5 mixtures (Ref 43), the reaction product, $CeVO_4$, is found, which indicates destabilization in this case to be occurring by chemical reaction.

Nagaraj and Wortman (Ref 45) have compared CSZ versus YSZ and MSZ thermal barrier coatings in burner rig tests at 704 and 899 °C using 29.6 ppm of sea salt in air, and 1.93 vol% S and 32 ppm V in the fuel. Both APS and EB-PVD prepared coatings were tested, as well as EB-PVD coatings that had sputtered "seal" coats of HfO_2 (45 μm), Al_2O_3 (7.5 μm), or platinum (7.5 μm).

The MSZ thermal barrier coating suffered the most hot corrosion, with major amounts of $MgSO_4$ and minor amounts of magnesium vanadate being formed at both temperatures, although no spalling was observed. Both the APS and EB-PVD YSZ coatings survived the 899 and 704 °C test periods (400 and 200 h, respectively) without spalling or bond coat corrosion. However, extensive quantities of yttria vanadate were formed on the YSZ surface at both temperatures, with some yttrium sulfate also being produced at 704 °C. The APS and EB-PVD CSZ coatings both survived 400 h at 899 °C, but the APS CSZ spalled within 200 h at 704 °C. Only $CeVO_4$ and "free" CeO_2 were detected on the 899 °C CSZ surface, whereas the 704 °C CSZ surface showed mostly cerium sulfate, with only minor amounts of $CeVO_4$.

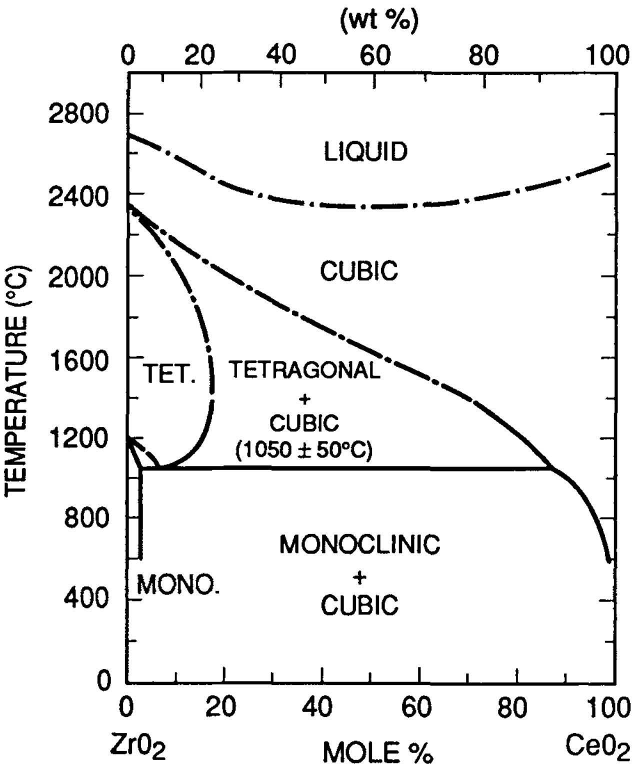

Fig. 4 Phase diagram of the CeO_2-ZrO_2 system according to Tani et al. (Ref 44). Source: Ref 41

It was found also that although the Al_2O_3-, HfO_2-, or platinum-sputtered seal coats themselves did not undergo chemical reaction, they were not impervious to salt penetration and failed to protect the underlying zirconia phase, as evidenced by corrosion at the sealant/zirconia interface in each case.

Since both the CSZ and YSZ coatings reacted to form the respective cerium or yttrium vanadate, these burner rig tests fail to show, in an absolute sense, whether CSZ or YSZ is "better" against vanadate hot corrosion. This illustrates the problem of obtaining discriminating corrosion tests: If the corrodent level (vanadium, in this case) is too low, then both coatings perform well; if it is too high (as it may be here), then both coatings fail. Obtaining the exact intermediate corrodent level at which the test becomes discriminating—that is, where the good coating passes and the poor coating fails—can be very difficult. However, these burner rig tests serve to define a level of contaminants at which it is known that both CSZ and YSZ will suffer hot corrosion by chemical attack. Moreover, they reconfirm that vanadium is the major problem, since the authors (Ref 45) point out that in essentially equivalent tests where vanadium was absent, YSZ coatings survived in excess of 1000 h of 927 °C cyclic burner rig testing without failure.

4.4.2 Scandia and India

Scandia (Sc_2O_3) and india (In_2O_3) have been identified from studies at the Naval Research Laboratory (NRL) as possible corrosion-resistant stabilizers for ZrO_2 TBCs. These oxides were selected as being more acidic than Y_2O_3 and therefore less likely to react with acidic vanadate melts than Y_2O_3 (Ref 24). Chemical studies confirmed that, as the pure oxide, both Sc_2O_3 (Ref 46) and In_2O_3 (Ref 47) are more resistant than Y_2O_3 to reaction with molten vanadates or SO_3-Na_2SO_4. In subsequent thermogravimetric (TGA)/SO_3 equilibrium experiments, a semiquantitative ranking of the resistance of the various ZrO_2-stabilizing oxides to reaction with molten vanadate-sulfate melts was established (Ref 17, 48), with the order of resistance being In_2O_3 > Sc_2O_3,CeO_2 > Y_2O_3,MgO.

In addition to corrosion resistance, however, the candidate oxides must have good "stabilizing ability," and this is not yet fully verified for Sc_2O_3 or especially In_2O_3. Sasaki et al. (Ref 49) have sought to quantify the stabilizing efficiency of the various oxides, and they rank $ScO_{1.5}$ and $InO_{1.5}$ as being less effective (at least for the T → M transformation) in stabilization than $YO_{1.5}$. The stabilizing action of Sc_2O_3 and In_2O_3 has also been concluded by Sheu et al. (Ref 10) to be different from that of Y_2O_3 or the other rare earth oxides. On the other hand, laboratory tests of APS-prepared Sc_2O_3-ZrO_2 TBCs have indicated Sc_2O_3 to be as good or better in stabilizing ability, and unequivocally better in vanadate hot corrosion resistance, than Y_2O_3 (Ref 50).

Although In_2O_3 shows the best resistance to reaction with V_2O_5, india-stabilized zirconia (ISZ) may prove to be questionable as a truly high-temperature, corrosion-resistant TBC material, although it may be usable at intermediate temperatures. During plasma spraying tests (Ref 51), ISZ lost In_2O_3 by volatilization and deposited as monoclinic ZrO_2. Also, ISZ has been found to be destabilized (probably by mineralization as with CeO_2) by molten sodium vanadate (Ref 47). On the other hand, if merited, ISZ coatings can be produced by electron-beam deposition (Ref 52), and the properties of ISZ might also conceivably be improved by better processing, especially the temperature firing regimen, during preparation of the plasma spray powder. In their study of In_2O_3-ZrO_2, Sasaki et al. (Ref 49) were able, for example, to prepare ZrO_2-$InO_{1.5}$ ceramics that allowed equilibrium studies at temperatures up to 1700 °C. Also, Sheu et al. (Ref 53) obtained the T′ phase in In_2O_3(8 mol%)-ZrO_2 by quenching from 1720 °C, which confirms that the desirable T′ phase, and presumably its superior thermomechanical properties, can be achieved in ISZ.

4.4.3 Ytterbia

Ytterbia (Yb_2O_3) has been reported by Stecura (Ref 54) as being an effective stabilizer for ZrO_2. Ytterbia is somewhat more acidic than Y_2O_3, and calculations using available thermodynamic data (Ref 55) indicate that, at 900 °C, a higher V_2O_5 activity is required for $YbVO_4$ (s) formation (9.3×10^{-10}) than for YVO_4 (s) formation (8.0×10^{-11}). However, both activities are quite low, especially when compared to Sc_2O_3 (6.9×10^{-5}). Assuming that it is indeed only the relative Lewis basicity of the stabilizing oxide that predominantly determines the TBC hot corrosion resistance, it is unlikely that Yb_2O_3 should be much superior to Y_2O_3 in conferring hot corrosion immunity, especially against vanadate-containing deposits.

5. Conclusions

Results of studies presently suggest that YSZ may be adequate for TBC applications where the corrodents are only sodium and sulfur (i.e., Na_2SO_4-SO_3 hot corrosion) and where the fuel sulfur content is 1 wt% or lower. Damaging penetration of Na_2SO_4 into the YSZ ceramic has not been reported (for aircraft-type operations) for either plasma-sprayed or EB-PVD-produced TBCs. Seal coating or laser glazing of the upper YSZ surface generally has not been found to be significantly effective. Although not reviewed here (since little work has been reported), the bond coat composition and structure may have an effect on TBC cycle life under corrosive conditions. One recent paper, for example, reports an improvement in TBC corrosion life by the use of a dual-layer bond coat (Ref 56).

Because of the strong reaction between Y_2O_3 and V_2O_5, YSZ is unlikely to be a suitable TBC material in engine environments containing appreciable vanadium. Scandia-stabilized zirconia (SSZ) currently appears to be the most promising TBC ceramic for improved vanadate hot corrosion resistance. Sufficient burner rig and engine test data are not available, however, to establish quantitatively how much improvement SSZ may give over present-day TBC materials, or whether the additional cost for Sc_2O_3 would be justified.

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