TECHNICAL ARTICLE

Developments in Thermodynamic Models of Deposit-Induced Corrosion of High-Temperature Coatings

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Degradation caused by silicate deposits limits the lifetime of protective coatings in gas turbine engines. In order to design more durable coating materials and architectures it is important to understand the behavior of ingested debris leading to the formation of deposits on component surfaces, and the subsequent reaction of those deposits with the coating materials. This article reviews recent advances in thermodynamic models and databases capable of predicting these reactions. It also describes the development of modeling approaches to capture key features associated with the intrinsic behavior of debris and deposits, their interaction with dense environmental barrier coatings, and reactions occurring during infiltration of molten deposits into porous or segmented thermal barrier coatings.

INTRODUCTION

The development of new coating materials and architectures able to mitigate the deleterious effects of corrosive deposits is critical to enable safe and reliable operation of current and future gas turbines.^{1,2} These deposits originate from ingested environmental debris typically comprising combinations of chlorides, sulfates, and oxides from seawater, dusts, volcanic ashes, and industrial emissions. Within the engine, non-oxide debris may decompose, and certain components may selectively volatilize as hydroxides or other gaseous species. Some debris particles will melt and adhere to component surfaces while others pass through the engine largely unaffected. The details of these processes, illustrated in Fig. 1, depend on the thermal properties of the particles (e.g., melting temperature, enthalpy of fusion, thermal conductivity), and factors such as the particle size, residence time, and inertia.^{3–8} The resulting deposits may deviate significantly from the composition of the ingested debris, and they may be partially or

fully molten. Depending on the melt viscosity and the surface tension, they may spread across the component surface and wick into porosity present in protective coatings on the component surfaces.

More than two decades of study on the degradation of thermal and environmental barrier coating (TBC and EBC) materials by silicious CMFAS* deposits have advanced the understanding of the coupled thermo-chemical and -mechanical mechanisms leading to accelerated coating failure.^{2,9–17} The majority of this work has focused on rare earth (RE) zirconate, silicate, and aluminate materials owing to their advantageous property combinations for use as protective coatings. Infiltration of the molten deposit into porous or segmented coating microstructures reduces the coating compliance. Reactions between the coatings and deposits can produce phase assemblages with increased thermal expansion (CTE) mismatch with the substrate. These processes magnify the thermal stresses upon cooling, leading to cracking and eventual delamination of the coatings. Several promising mitigation

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*The compositions are designated by the first letter of the oxide cation, i.e., C = CaO, M = MgO, Fe = FeO_x, A = AlO_{1.5}, S = SiO₂. CMFAS is used in place of the more common acronym CMAS to reflect that most in-service deposits contain iron. Deposit compositions herein are defined using subscripts to indicate the molar percentages of cations in the deposit, e.g., C₃₁M₉F₅A₁₂S₄₃ contains 12 mol% AlO_{1.5} and 43 mol% SiO₂.

strategies have been developed. Most rely on modifying the composition of the coating material to either favor reactions that consume the deposit melt and block pathways for melt infiltration into porous TBCs,^{18,19} or to minimize the reactivity between dense, impenetrable EBCs and surface deposits.^{20–22} In both cases, calcium rare earth oxyapatite [nominally $\text{Ca}_2\text{RE}_8(\text{SiO}_4)_6\text{O}_2$] has been identified as an important reaction product that exists in equilibrium with a broad range of CMFAS deposit compositions. Tailored porosity, non-wetting surface structures or materials, and non-reactive, impermeable metallic layers also provide benefits, as long as those structures are stable in the operating environment.^{23–25} The implementation of layered architectures combining sacrificial CMFAS-mitigating outer layers with more mechanically or environmentally resistant inner layers can enable resilient multifunctional performance.^{12,26–29}

There is also growing evidence that CMFAS-type deposits also degrade superalloys and metallic bond coats.^{30–35} Unlike classic Na_2SO_4 -induced alloy hot corrosion, which subsides above 900°C as the deposit evaporates, the persistence of mixed-anion (oxide, chloride, sulfate) CMFAS deposits to higher temperatures presents a significant durability challenge to overcome in advanced alloy designs. The nascent understanding suggests that the deposit constituents (in solid, liquid, or vapor states) react vigorously with protective $\text{AlO}_{1.5}$ thermally grown oxide (TGO). The TGO is converted into less-protective aluminates and silicates, accelerating oxidation of the underlying alloy, and topcoat spallation. However, given the broad deposit composition space and complexity introduced by vapor-phase

reactions, many questions remain about the relative importance of the cation and anion constitution, and gas atmosphere, on the stability of mixed-anion deposits and subsequent coating degradation.

The progression and severity of the deposit-induced degradation depends on the intrinsic behavior of the debris within the hot gas path, the tendency to form surface deposits, and the degree of infiltration into and interaction with the TBC, EBC, or TGO material. Each stage of this process (Fig. 1) is governed by thermodynamic driving forces that control reactions and melt flow. Experimental investigations systematically comparing multiple deposit compositions and coating material combinations have contributed important insights into the effects of the deposit and coating composition, temperature, and microstructure.^{12,13,22,36–40} However, the expansive range of deposit compositions and operating conditions makes it impractical to experimentally test all possible scenarios, particularly when screening new coating material candidates.

To overcome this limitation, recent efforts have focused on elucidating the underlying phase equilibria and thermodynamic properties for key subsystems.^{41–46} The intent is that computational thermodynamics models based on these insights could be used alongside thermophysical property and fracture mechanics models in an integrated framework to predict coating performance,^{2,12,13,17} in the spirit of integrated computational materials engineering (ICME).⁴⁷ Such a framework (Fig. 2)

Fig. 1. Sequence of steps leading to formation of surface deposits from ingested debris.

Fig. 2. Framework identifying key features of the deposit formation and interaction with coatings.

provides benefits in identifying coating compositions to mitigate degradation caused by specific ranges of deposit compositions, or to select conditions that maximize the knowledge generated by a limited number of targeted experiments. The promise of this approach has been demonstrated in a series of investigations focused on yttrium disilicate ($\text{Y}_2\text{Si}_2\text{O}_7$, YDS) EBCs.^{40,48,49} Opportunities exist to implement similar models for other EBC and TBC systems. This article reviews the development and capabilities of the thermodynamics databases underpinning this framework, and highlights opportunities for future advancement.

MODELS AND THERMODYNAMIC DATABASES

Modeling Needs and Approaches

The modeling needs can be divided into two categories. First is the need to understand the intrinsic behavior of the ingested debris and accumulated deposits. Key properties influencing the tendency to adhere, wet, and infiltrate a coating include the liquidus and solidus temperatures, the melt fraction and composition at the component surface temperature, and the thermophysical properties (viscosity, surface tension, etc.) of the resulting liquid. The second category encompasses reactions occurring between the deposit and the coating materials.

The general characteristics of the deposits can be described using basicity indices that capture the effect of the relative fractions of alkali components (e.g., CaO, MgO, etc.) and more acidic components such as SiO_2 on the characteristics of the liquid phase.^{50–56} These approaches, which were originally developed to describe glassmaking processes and the behavior of metallurgical slags and fluxes, can provide general insights into the melt properties, including the degree of network-connectedness (and thus viscosity). They also provide information about the tendency for a silicate melt to react with crystalline oxides based on relative differences in basicity. For instance, a coating would be more likely to react with a deposit that had a large difference in basicity relative to the oxides comprising the coating. However, these indices do not provide direct insight into the melting temperatures or the identity of the reaction products. This limits their utility to model important details of the degradation process. Additional insight can be gained by using computational thermodynamics models, described below. These models are capable of predicting melting and decomposition temperatures, liquid compositions, reaction driving forces, and related features. The melt composition can then be used as an input for empirical models to determine properties such as the temperature-dependent melt viscosity^{57,58} or the thermal expansion coefficients for the glasses formed when the melt is cooled.⁵⁹

When a molten deposit is formed on a TBC or EBC, the coating will invariably begin to dissolve into the melt owing to the fact that virtually all coating-relevant oxides have some degree of solubility in silicate melts. The subsequent reactions, which often form reaction products listed in Table I, can be divided into three categories. First, upon saturating the melt, the coating constituents can reprecipitate with the same or a slightly modified composition. For instance, coatings in the $\text{REO}_{1.5}\text{-ZrO}_2$ system commonly dissolve and reprecipitate with a lower $\text{REO}_{1.5}$ concentration than the original coating, due in part to the higher $\text{REO}_{1.5}$ solubility in the melt compared to ZrO_2 . The reactions can also form products incorporating significant fractions of components from both the coatings and the deposit. Termed reactive crystallization for their ability to crystallize molten deposits, this second category of reactions underpins mitigation strategies for RE-based TBCs, but also drives the undesirable consumption of dense EBCs. The apatite phase is the most reported and studied reactive crystallization product, but a variety of other silicates and aluminosilicates listed in Table I have also been observed. In the third category, the melt may crystallize any number of phases comprising primarily components initially in the deposit. This intrinsic crystallization process can occur either due to changing melt composition caused by reactive crystallization, or changes in temperature based on the service conditions, or as the melt infiltrates down the thermal gradient through the coating thickness.

Subtle changes in the solubility and reservoir of specific reactants in the deposit, and their tendency to partition between phases, can have a profound influence on the stability of various reaction products. For instance, slight changes in the deposit composition can cause changes of more than 100°C in the solidus temperature, depending on which eutectic the composition falls into.³⁷ Likewise, the trend for larger RE cations to stabilize apatite while smaller RE cations are more likely to stabilize the garnet phase or partition back into the reprecipitating ZrO_2 -based phase significantly changes the volume of the reactive crystallization products formed. Because these factors ultimately dictate the severity of the degradation process or the effectiveness of a given mitigation strategy, there is a critical need to develop models capturing the interplay between coating material, deposit composition, and service conditions on the reaction sequence. Computational thermodynamics represents the most promising approach to achieve this vision in the near term, although other data-driven approaches may provide additional value in the future.

Table I. Common reaction products between silicate deposits and ceramic coatings, adapted from Ref. 2.

Category	Name	Abbreviation	Nominal formula
Deposit and intrinsic crystallization	Anorthite	An	$\text{CaAl}_2\text{Si}_2\text{O}_8$
	Diopside	D	$\text{CaMgSi}_2\text{O}_6$
	Cristobalite, Tridymite	S	SiO_2
	Liquid (glass)	L	—
	(Pseudo-)wollastonite	CS	CaSiO_3
	Calcium Silicate	C_2S	Ca_2SiO_4
	Melilite	M	$(\text{Ca})_2(\text{Al,Mg})(\text{Al,Si})\text{SiO}_7$
Reprecipitation	Spinel	Sp	MgAl_2O_7
	Fluorite	F	$(\text{Zr,RE,Ca})\text{O}_{1.5}$
	Tetragonal ZrO_2	t	$(\text{Zr,RE,Ca})\text{O}_{1.5}$
Reactive crystallization	Zircon	ZS	ZrSiO_4
	RE disilicate	REDS	$\text{RE}_2\text{Si}_2\text{O}_7$
	RE monosilicate	REMS	RE_2SiO_5
	Calcium Zirconate	CZ	CaZrO_3
	Apatite	Ap	$(\text{Ca,RE})_4(\text{RE,Zr})_6(\text{SiO}_4)_6\text{O}_2$
	Garnet	G	$(\text{Ca,RE,Zr})_3(\text{Zr,Ti,Mg,Al,Fe})_2(\text{Si,Al,Fe})_3\text{O}_{12}$
	Cuspidine	C	$(\text{RE,Ca,Hf,Mg})_4(\text{Si,Al})_2\text{O}_{9.5}$
	Cyclosilicate	CS	$\text{Ca}_3\text{RE}_2\text{Si}_6\text{O}_{18}$, $\text{Ca}_2\text{ZrSi}_4\text{O}_{12}$
	Silicocarnotite	SC	$\text{Ca}_3\text{RE}_2\text{Si}_3\text{O}_{12}$

Computational Thermodynamics Models for Phase Equilibria and Reactivity

Computational thermodynamics approaches employing the CALPHAD (CALculation of PHase Diagrams) method provide a powerful and efficient framework for modeling the behavior of multicomponent, reacting systems.^{60,61} Leveraging the relationship between the Gibbs energies for individual phases and the overall phase equilibria for a system, the technique is used both to assess the thermodynamic properties of phases (i.e., to build databases) and to predict the behavior of higher-order systems. The assessment approach integrates data from multiple experimental and ab initio techniques, increasing the collective value of scarce or difficult to obtain thermodynamic data, while also facilitating the identification of errant data.⁶⁰ From these assessed thermodynamic functions, it is possible to predict phase equilibria, reaction driving forces, and properties such as temperature-dependent molar volume (and thus thermal expansion behavior) and the viscosity of liquid phases.

In this method, the Gibbs energy functions describe the effects of temperature, pressure, composition, and other natural variables on the lattice stability of each phase. Adjustable interaction parameters are introduced to account for the excess contribution to the Gibbs energy to account for deviations from ideal mixing of the endmembers. Models for solution phases employ the compound energy formalism to represent the behavior of components on sublattices corresponding to the structure of crystalline phases, or the chemical configurations in liquids or non-crystalline phases.⁶² Separate interaction parameters are

defined for each component on each sublattice in which it resides for each phase. Numerical values for the interaction parameters are estimated and then refined by fitting available data. A wide variety of thermodynamic property data (e.g., formation and mixing enthalpies, chemical activities, heat capacities, etc.) and phase equilibria data (e.g., melting temperatures, equilibrium phase assemblages and compositions, partition coefficients, etc.) can be used. By using multiple data types or data points to fit each parameter, the least-squares fitting approaches can account for the relative uncertainty in each input value to arrive at the best fit. Assuming that assessments of individual binary and ternary sub-systems are performed in a manner to produce databases of self-consistent models and parameters, they can be extrapolated to predict the behavior of higher-order systems.

A number of software packages exist to use the CALPHAD method to perform parameter assessments and subsequent thermodynamic calculations to predict system behavior. These include commercial packages such as FactSage,^{63,64} Thermo-Calc,⁶⁵ and PANDAT,⁶⁶ and open-source packages such as OpenCalphad⁶⁷ and pycalphad.⁶⁸ The ability to use these tools to model the behavior of CMFAS-type deposits and their interaction with TBC and EBC materials is contingent on the capabilities of the available databases. This modeling requires a comprehensive database with robust models for the sub-systems containing the components of the deposits (to predict the behavior of the deposits) and for both the deposits and coating materials to model reactions with coatings. Based on the range of elements included, the FToxid database available within the

FactSage package⁶⁴ and the TCOX databases available with the Thermo-Calc system⁶⁹ have proven most effective for this purpose. The capabilities and recent developments in these databases are elaborated in the following Sections.

FactSage FToxid (FACT Oxide Database)

The FToxid database, which is part of the FACT solutions database package, has robust descriptions for the quinary CMFAS oxide system. It also contains partial descriptions of systems encompassing an additional 19 cations (As, B, Ba, Co, Cr, Cu, Ge, K, Li, Na, Mn, Ni, P, Pb, Sn, Sr, Ti, Zn, and Zr) as oxides and, in some cases also as sulfates and various salts.⁷⁰ This database can be used in conjunction with the compatible FactPS pure substances and compounds database to model the behavior of deposits involving solid-state and gas-phase reactions with key sulfates (e.g., Na₂SO₄, CaSO₄, etc.) and chlorides, and their dissolution into molten oxides, and gas-phase reactions. Given the variety of compositions modeled, this database is particularly well-suited to model the characteristics of representative debris and deposits, including those deposits with small fractions of alkali and alkali-earth cations. For instance, it has been used to understand the melting behavior of specific debris sources, e.g., sands or ashes, and to identify ranges of molten- and semi-molten deposits across the CMFAS composition space.^{2,13,39,71} It has also been used to extract specific thermodynamic parameters such as the volatility of deposits in a water vapor environment,³³ or to model the viscosity of deposits using built-in empirical relationships.⁷²

Despite its excellent capability for modeling the intrinsic behavior of the corrosive deposits, the FToxid database has limited capability to model interactions between deposits and most coating materials. Specifically, although the database contains models for the equilibria in the binary systems containing alumina and various REO_{1.5}, the REO_{1.5} are not modeled in any ternary systems. Additionally, the liquid model used for the AlO_{1.5}-REO_{1.5} systems is incompatible with the model used for the silicate-based liquid phase.⁷⁰ However, there are efforts underway to develop new liquid-phase models incorporating REO_{1.5} in the silicate-based liquid phase⁷³ that could expand the capability of future versions of this database.

Thermo-Calc Software TCOX (TCS Metal Oxide Solutions)

Over the past decade, the Thermo-Calc TCOX metal oxide solutions database has been expanded from 8 cations (CMFAS + Cr, Mn, and Ni in version TCOX4) to 21 cations (CMFAS + Co, Cr, Cu, Gd, La, Mg, Mn, Mo, Na, Nb, Ni, P, Ti, V, W, Y, and Zr in the most recent version TCOX10.1).⁶⁹ Notably, this database implements a two-sublattice model for the ionic liquid phase to account for the relative

	C ₃₃ Mg ₉ A ₁₃ S ₄₅	C ₃₆ A ₁₄ S ₅₀	C ₂₄ A ₁₇ S ₅₉	C ₁₅ A ₁₅ S ₇₀
Y ₂ SiO ₅				
Ex.	L/t	L/t	L/t/ZS	L/ZS
5.1	L/t	L/t/CS*	L/t/ZS/An	L/ZS/An
6	L/t	L/t/CS*	L/t/ZS	L/ZS/An*
7	L/t	L/t/CS*	L/t/ZS	L/ZS/An*
10	L/t/F*	L/t/CS*	L/t/ZS	L/ZS/An*
Y ₄ Zr ₃ O ₁₂				
Ex.	L/F/Ap	L/F/Ap	L/F/Ap	L/ZS/Ap
5.1	L/F	L/F	L/YDS/t/An	L/ZS/YDS/An
6	L/F/Ap/SC*	L/Ap/t/SC	L/t/Ap	L/ZS/Ap
7	L/F/Ap/M*	L/F/Ap	L/F/Ap	L/ZS/Ap
10	L/F/Ap/M*	L/F/Ap	L/F/Ap	L/ZS/Ap
Y ₂ O ₃				
Ex.	G/Ap/M	L/Ap/SC/An	L/Ap/An	L/Ap/YDS
5.1	L/YMS	L/YMS	L/YDS/An	L/An/YDS
6	L/Ap/SC/M/Sp*	L/Ap/SC	L/Ap	L/Ap/YDS
7	L/Ap/SC/M/Sp	L/Ap/SC	L/Ap	L/Ap/S
10	L/Ap/SC/M/Sp	L/Ap/SC	L/Ap	L/Ap/YDS
Gd ₂ Zr ₂ O ₇				
Ex.	L/F/Ap	L/Ap/t	L/Ap/t/ZS	L/Ap/ZS
7	L/F/Ap	L/Ap/t	L/Ap/ZS/An/t*	L/Ap/ZS/An
10	L/F/Ap	L/Ap/t	L/Ap/ZS/An/t*	L/Ap/ZS/An
Gd ₂ O ₃				
Ex.	L/Ap/Sp/M	L/Ap/M	L/Ap/An	L/Ap/An/S
7	Ap/M/Sp	L/Ap/M*/SC*	L/Ap/An	L/Ap/An/S
10	Ap/M/Sp	L/Ap/M*/SC*	L/Ap/An	L/Ap/An/S
<div> <div> <div>↑ TCOX version</div> <div>5µm</div> </div> <div> <div>* Less than 5 mol% present</div> </div> <div> <div>Agreement between ex. and calculated equilibrium phases:</div> <div> <div>Poor</div> <div>Moderate</div> <div>Good</div> </div> </div> </div>				

Fig. 3. Comparison between observed and predicted phase assemblages formed by the reaction between Y- and Gd-zirconates and -oxides and four CMFAS deposits at 1300°C. In all cases, 25% of the cations come from the coating material and the remainder from the deposit. Calculations were performed using Thermo-Calc database versions TCOX5.1, TCOX6, TCOX7, and TCOX10; Gd was not included prior to TCOX7. Experimental (ex.) results adapted from Ref. 39. The 5-µm scale bar applies to all micrographs unless otherwise noted; phase name abbreviations defined in Table I.

network-forming and -modifying tendencies of various oxides.^{74,75} This approach can capture the amphoteric nature of alumina in silicate melts, i.e., as either a component in the silicate network or as an ionic modifier. It also provides an improved capability to model the liquid immiscibility in the ternary $\text{AlO}_{1.5}$ - SiO_2 - $\text{REO}_{1.5}$ and extrapolated higher-order systems.^{76–79} The ability of this liquid model to predict the degree of network-connectedness in the melt has also been leveraged in recent versions of the database to improve models of melt viscosity.⁸⁰

Interest in using this database to model the interaction of TBCs with silicate melts first emerged when descriptions for the $\text{YO}_{1.5}$ and ZrO_2 systems were added to the database in version TCOX5.1.⁸¹ To assess the capabilities of the database for modeling these interactions, systematic experiments were performed to assess the equilibrium between a variety of coating materials and constituents (e.g., ZrO_2 , $\text{YO}_{1.5}$, 7YSZ, and $\text{Y}_4\text{Zr}_3\text{O}_{12}$) and four deposits spanning a range of representative compositions.³⁹ Comparison between the calculated and experimentally observed equilibrium phase assemblages showed that the database could accurately predict the equilibria in some cases involving ZrO_2 -rich TBC compositions (examples shown in Fig. 3). However, the predictions were less accurate at higher $\text{YO}_{1.5}$ concentration because the $\text{CaO-SiO}_2\text{-YO}_{1.5}$ subsystem, which contains the apatite phase, was not assessed in TCOX5.1. Based in part on an experimental investigation of phase stability in that system to determine the solid solution behavior and melting points of key phases,⁴¹ an assessment of the $\text{CaO-SiO}_2\text{-YO}_{1.5}$ system was included in the subsequent TCOX6 version.⁸¹

The accuracy of the predictions of the CMAS + TBC equilibria from TCOX6 improved considerably compared with TCOX5.1 (Fig. 3), but discrepancies are observed related to excess partitioning of $\text{YO}_{1.5}$ into apatite rather than the ZrO_2 -based phases t - ZrO_2 and fluorite. This tendency reflected an inconsistency between the relative chemical potential of $\text{YO}_{1.5}$ in the silicate vs zirconate systems in the models. Given that the thermochemistry of the $\text{SiO}_2\text{-YO}_{1.5}$ system is well studied owing to its importance for EBCs,^{46,82} knowledge of termini of three-phase fields (i.e., those with fixed chemical potential) involving the silicates and solid solutions in the $\text{YO}_{1.5}\text{-ZrO}_2$ binary⁴² can be used to link the assessments of the binary systems. Using such data, the relevant subsystems were reassessed in TCOX7.⁸³ In general, predictions based on the TCOX7 database show good agreement with observed equilibria between the silicate deposits and coating materials containing $\text{YO}_{1.5}$ and ZrO_2 (Fig. 3). The most notable exception arises for deposits with higher concentrations of MgO , $\text{AlO}_{1.5}$, and FeO_x , which promote the formation of multicomponent aluminosilicates with the garnet

structure, e.g., $\text{C}_{33}\text{Mg}_9\text{Al}_{13}\text{S}_{45} + \text{YO}_{1.5}$ in Fig. 3. A preliminary experimental assessment of the stability of this phase in the Y + CMAS system was recently reported.⁴⁴ However, the complexity of the phase, which contains multiple cations spread across three distinct cationic sites, complicates the thermodynamic modeling based on the available data. A reliable description is not yet available in a commercial thermodynamic database.

Owing to the interest in coatings based on $\text{Gd}_2\text{Zr}_2\text{O}_7$,^{12,18,84–86} parallel efforts focused on elucidating the equilibria in the key subsystems linking the $\text{GdO}_{1.5}\text{-ZrO}_2$ system to the CMFAS systems.^{42,43,87–89} These formed the basis for the addition of the $\text{GdO}_{1.5}$ to TCOX database in version TCOX7. Calculations with this database can accurately predict the equilibria for reactions forming apatite and fluorite in equilibrium with molten CMFAS, which are most critical for understanding coating degradation. However, the stability of anorthite appears to be overpredicted in some cases.

Subsequent releases of the TCOX database (i.e., TCOX8, TCOX9, and TCOX10) have made small adjustments to core systems relevant for modeling CMFAS-TBC and -EBC interactions. These recent database expansions added a large number of additional oxide components, significantly improving the capabilities of the database to model the intrinsic behavior of more complex deposit chemistries. Therefore, only the most recent (TCOX10) is included in the comparison between the experiments and predicted equilibria in Fig. 3. With the exception of the lack of a description for the garnet solid solution, and small inconsistencies in the stability of anorthite, the predictions from the TCOX10 database are generally consistent with experimental data. Additionally, the TCOX10 database also includes an improved model for silicate melt viscosity that connects directly to the underlying melt structure in terms of changes in the relative concentrations of network-forming vs -modifying species as a function of the liquid composition and temperature. Based on preliminary assessments, it appears that this approach could be used to provide highly reliable predictions of the deposit melt viscosity.⁸⁰

MODELING STRATEGIES FOR COATING PERFORMANCE ASSESSMENT

When considering the reactions underpinning deposit-induced degradation processes, the key questions relate to (i) whether debris will melt and adhere to components along the gas path, (ii) how the deposit characteristics will evolve with time, and (iii) to what degree the deposit will react with the coating material either on the surface or during infiltration into porosities within the coating. The computational thermodynamics models described in the prior Section are capable of providing important insights to assist in answering each of these

questions for various deposit and coating compositions, and service conditions. The following Sections review some recently developed and applied modeling approaches, and also provide case studies illustrating opportunities for future model development.

Intrinsic Behavior of Debris and Deposits

Debris Melting and Deposit Adherence

The first important question is whether a particular debris source will melt, and what the composition of the formed melt will be. A number of studies have used the FactSage or Thermo-Calc databases to predict either the melting behavior of specific individual deposits or across broad ranges of potential debris compositions.^{2,12,13,17,39,90} The latter has proven useful in the identification of ranges of representative deposits corresponding to the limits of the expected extent of deposit melting. These are typically simple point equilibrium, step (vs temperature), or mapping type calculations that are readily performed with various software packages described in Sect. 2.2.

Stability and Decomposition of Complex Mixed-Anion Deposits

There is a growing recognition that mixed-anion (e.g., oxide + sulfate) deposits, especially those containing significant fractions of CaSO_4 , are important both for the degradation of ceramic coatings^{91–93} and in accelerating alloy oxidation.^{30,31,34,35} Under some conditions, the sulfate components in the deposit will decompose rapidly, generating a transient increase in the gaseous SO_x concentration as the deposit converts into a conventional oxide deposit. In other cases, the sulfate components may remain in the deposit for a longer duration, where they may directly impact alloy durability. The stability of the mixed-anion deposit depends on the operating conditions (gas atmosphere, temperature) as well as the presence of non-equilibrium mixtures of sulfates and oxides that may react and drive evolution in the deposit constitution.

These behaviors can be modeled using available computational thermodynamics databases that include the relevant oxide and sulfate phases, and gaseous species. To illustrate these effects, a series of calculations were performed using various sulfate-containing deposit compositions. In these calculations, the temperature-dependent phase equilibrium, including gas-phase speciation, was calculated at a fixed oxygen partial pressure (0.21 atm) and fixed system size. Thus, the calculations represent equilibrium conditions above the deposit without the removal of gaseous decomposition products. The first calculation investigated the behavior of pure CaSO_4 . The results showed that between room temperature and 1525°C the solid CaSO_4

Fig. 4. Predicted (a) temperature-dependent sulfate decomposition and (b) corresponding gaseous SO_2 partial pressure above pure CaSO_4 , CaSO_4 in contact with $\text{AlO}_{1.5}$, and mixed-anion CMFAS deposits. In this example, 1/3 of the Ca and Mg in the CMFAS deposits are supplied by CaSO_4 and MgSO_4 , respectively, and the remaining cations are initially present as oxides.

remains stable [Fig. 4a]. The partial pressure of SO_2 (and, by relation, SO_3) rises slowly with increasing temperature [Fig. 4b] but remains low enough to prevent significant decomposition of the CaSO_4 under the conditions studied. The implication is that in the temperature range relevant for hot corrosion, pure CaSO_4 would decompose slowly in flowing gas.

The next set of calculations was based on a mixture of 50 mol% $\text{AlO}_{1.5}$ and 50 mol% CaSO_4 to simulate the potential reaction between CaSO_4 and an alumina TGO on an alloy. The results are also shown in Fig. 4. In this case, the driving force to form calcium aluminate phases destabilizes the CaSO_4 resulting in higher SO_x partial pressures. The calculations also predict that the CaSO_4 in the mixed $\text{CaSO}_4 + \text{Al}_2\text{O}_3$ deposit would decompose at lower temperatures. In this closed system, the decomposition of CaSO_4 is expected above 1300°C, although the decomposition temperature would drop in a system with significant gas flow to sweep away the evolved gaseous species. A final set of calculations examined the behavior of three mixed oxide-sulfate CMFAS deposits. Here, the cation

ratios in the three deposits were adopted from prior studies⁴⁹ to reflect a range of relevant behaviors. The deposits were defined with one third of the Ca and Mg cations coming from sulfates and the remainder of the deposit from oxides. The calculations (Fig. 4) showed that the reaction between the (Ca,Mg)SO₄ and other oxides in the deposit further destabilizes the sulfates, leading to significantly higher SO_x partial pressures and much lower predicted temperatures for complete sulfate decomposition. This effect appeared to be the most pronounced for the SiO₂-rich, CaO-lean deposit compositions. Analysis of the equilibrium phases formed suggested that this composition-dependent effect is associated with the strong driving force to form calcium silicates.

Reactions with Dense Environmental Barrier Coatings

EBCs are typically deposited with a nominally dense microstructure to inhibit ingress of gaseous oxidants. Thus, accelerated failure occurs due to increased thermal stresses caused by the progressive conversion of the coating material into phases with increased thermal expansion mismatch with the substrate compared with the coating itself. For instance, conversion of yttrium and ytterbium disilicate to apatite generates tensile stress and channel cracking upon cooling due to the increased CTE mismatch between the SiC substrates and apatite.^{17,49,94} Melt infiltration and subsequent stiffening of the coating are not the major drivers for thermomechanical failure of EBCs, but may contribute to blistering-type failure associated with combined reactions and grain boundary penetration.^{95,96}

The typical reaction progression for EBCs exposed to CMFAS deposits is shown in Fig. 5. In

the first stage of the process, the coating dissolves into the melt, increasing the total volume of the melt [Fig. 5]. Once the melt is saturated with the coating constituents, crystalline reaction products (e.g., apatite) begin to precipitate. In one scenario, the reactions will continue until thermodynamic equilibrium is reached between the coating and residual molten deposit, but with a significant fraction of melt remaining. This behavior, illustrated in Fig. 5c, is common with RE disilicates for which the reactions often involve exchange of Si (from the coating) with Ca (from the melt), but with little net change in the melt volume. In the second scenario, illustrated in Fig. 5d, the molten deposit is entirely consumed by the reactions, at which point the reaction rate would be significantly diminished. This behavior is expected for RE monosilicates and aluminates for which the crystallization reactions involve consumption of both Ca and Si from the melt.

Based on this understanding, mitigation strategies include (i) identifying coating materials that exhibit low reactivity with a wide range of deposits, (ii) designing the coating to maximize the amount of deposit consumed per mole of coating reacted, (iii) identifying materials that readily form dense, impermeable reaction product layers to slow the reaction with the underlying coating, or (iv) implementing multi-layer structures with a sacrificial outer layer protecting the inner EBC. The thermodynamic simulations described in this Section are directly applicable to the first two strategies listed. For the third, the morphology of the reaction layer is more important than the reaction products. In that case, phase equilibrium calculations provide utility for determining the relative change in melt volume, since reactions that reduce melt volume would be more likely to form protective reaction layers without liquid (glass) surrounding grains of

Fig. 5. The interaction of (a) a dense EBC with a molten silicate deposit typically involves a stage of (b) coating dissolution and (c) the growth of a reaction product layer. Depending on the system, the reaction may cease due to the establishment of thermodynamic equilibrium between the coating and residual melt, or (d) consumption of the remaining liquid.

the crystalline reaction product. The proposed CMFAS-resistant top coat architectures used as part of the fourth strategy are typically similar to the TBCs, which are discussed in the following Section.

Based on the reaction sequence observed in typical experiments, one approach to model the consumption of the coatings involves setting up automated, sequential phase equilibria calculations for systems containing incremental additions of the EBC material to a fixed initial quantity of the deposit. Assuming that diffusion is sufficiently fast in the melt to maintain pseudo-equilibrium within the molten deposit, these calculations correspond to progressively increasing the thickness of the reacted coating (denoted δ in Fig. 5). These calculations are typically performed on a molar basis, but the results can be re-cast using molar volumes in terms of the thicknesses of the residual deposit and reaction layers, relative to the initial deposit thickness (denoted h in Fig. 5). To accomplish this, the calculated molar fractions can be normalized using the molar volumes of each phase. Two parameters emerge. The first is the normalized recession depth, δ , which can be calculated using Eq. 1. The second is the normalized effective thickness of each reaction product phase, χ_{RP} , which is calculated with Eq. 2. The latter represents the contribution of each phase in the deposit and reaction layer (e.g., liquid, apatite, crystalline SiO_2 , etc.). For these calculations, M is the number of moles, V_m is the molar volume, and i represents the initial deposit. The sum of χ_{RP} for all phases represents the combined instantaneous thickness of the deposit and reaction layers, normalized by the original deposit thickness.

$$\delta = \frac{M_{\text{YDS}} V_{m,\text{YDS}}}{M_i V_{m,i}} \quad (1)$$

$$\chi_{\text{phase}} = \frac{M_{\text{phase}} V_{m,\text{phase}}}{M_i V_{m,i}} \quad (2)$$

This calculation strategy has been effectively applied to study how factors including temperature, deposit composition, and coating composition effect maximum expected recession (δ_{max}) of yttrium silicate EBCs. The effort first focused on validating the modeling strategy based on reactions between YDS (as coatings and sintered pellets) and the $\text{C}_{31}\text{M}_9\text{F}_5\text{A}_{12}\text{S}_{43}$ oxide deposit at 1300°C .⁴⁹ The results showed good agreement between experimental data and model predictions for both the recession depth and evolving melt composition. A subsequent investigation considered an expanded range of deposit compositions and included the effect of temperature.⁴⁰ This effort identified that the Ca:Si ratio in the deposit is a key determining factor governing the thickness of coating consumed by the reactions. These investigations also showed that because the reactions are fast, likely facilitated by

the constant presence of melt at the reaction interface, the final thermodynamic equilibrium is reached in a timescale much shorter than the expected component life. Thus, the thermodynamic simulations provide significant utility even though they don't capture the reaction kinetics explicitly. Subsequent work showed that the calculations could be automated to readily sample hundreds of deposit compositions. Subsequent integration with mechanics models facilitates the prediction of scenarios in which coating failure would be primarily thermochemical (i.e., consumption of the coating) or thermochemical (i.e., due to thermal stress induced cracking).¹⁷

The same modeling approach was applied to investigate the reactivity of YMS with a variety of representative deposit compositions.⁴⁸ The results suggest a different reaction progression: CaO-rich melts still react with the coating material to form apatite, while CaO-lean (and SiO_2 -rich) melts tend to form YDS as a reaction product. The two reactions can happen in tandem, maintaining the melt composition in a range that allows for significant reaction depth. However, because these reactions consume the melt, the predicted end state corresponds to Fig. 5d, rather than Fig. 5c. Additionally, these melt-consuming reactions appear more likely to form a dense reaction layer that significantly slows the reaction rate. Here again, even though the thermodynamic models do not explicitly consider the reaction kinetics, they do provide clues about the likely kinetic regime for a given reaction pathway.

Reactions with Porous Thermal Barrier Coatings

The primary CMAS-induced TBC failure mode is related to densification and loss of compliance in the infiltrated ceramic top coat. Depending on the architecture of the coating and the properties of the substrate, the elevated thermal stresses upon cooling (and subsequent thermal cycling) produce combinations of channel cracking and near-surface or deep delamination cracking.^{9,10,12,13,15,16,97,98} Because the strain energy available to drive cracks increases with the thickness of the stiffened layer, it is desirable to minimize infiltration. For mitigation strategies relying on reactive crystallization of the melt, the reactions must seal the infiltration channels on a timescale faster than that required for significant melt infiltration. The competition between infiltration and sealing depends on (i) variations in the melt viscosity, (ii) the rate of coating dissolution, (iii) the constitution of the reaction products, and (iv) their growth rate and morphology. Each of these factors is influenced by the reaction temperature, the identity of the TBC material, and the composition of the deposit.

To facilitate understanding these processes, thermodynamic modeling can be used to predict the

Fig. 6. As (a) the silicate melt penetrates into pores, gaps, and cracks in the coating, reactions can lead to (b) a net decrease in the volume of crystalline material, driven by high solubility of the coating constituents, (c) limited net change in the crystalline volume due to combined dissolution and precipitation, or (d) an increase in the net crystalline volume through reactive crystallization. It is desirable for the crystalline volume (V_{crys}) to be greater than the volume of TBC dissolved (V_{TBC}), i.e., $V_{\text{crys}}/V_{\text{TBC}} > 1$. This figure represents the typical microstructure of an EB-PVD TBC, but the reaction mechanisms are relevant to coatings produced by other methods.

equilibrium reaction products and changes in the melt composition (and thus viscosity) as the reaction between the deposit and the TBC proceeds [Fig. 6a]. This knowledge can be coupled with insights about the rates of coating dissolution, reaction product nucleation, and growth^{99–102} to assess the expected behavior of a given coating material. The efficacy of the reactions to block infiltration can be quantified in terms of the relative volume of crystalline material (V_{crys}) formed for a given volume of the TBC dissolved (V_{TBC}). If the TBC has significant solubility in the melt and crystallization is unfavorable, the reactions result in a net loss of solid material i.e., $V_{\text{crys}}/V_{\text{TBC}} < 1$, Fig. 6b. The widening of the channels in the coating via this process would accelerate infiltration. Conditions producing significant reprecipitation but limited reactive crystallization result in $V_{\text{crys}}/V_{\text{TBC}} \approx 1$. As shown in Fig. 6c, this would likely have a limited effect on the infiltration behavior beyond the effect of changing the fine microstructure along the gap surfaces on the capillary forces driving infiltration. Effective control of the infiltrated depth by sealing open channels requires $V_{\text{crys}}/V_{\text{TBC}} > 1$, as shown in Fig. 6d.

Based on this understanding of the infiltration and reaction process, it is desirable to identify

Fig. 7. Evolution of (a) the residual liquid fraction (normalized to the initial liquid content) and (b) the $V_{\text{crys}}/V_{\text{TBC}}$ for reaction between a $\text{C}_{31}\text{M}_9\text{F}_5\text{A}_{12}\text{S}_{43}$ deposit and TBCs based on 7YSZ, $\text{Y}_4\text{Zr}_3\text{O}_{12}$, or a notional $\text{YO}_{1.5}$ -rich composition containing 80 mol% $\text{YO}_{1.5}$ and 20 mol% ZrO_2 (denoted $\text{Y}_{80}\text{Zr}_{20}$). Increasing the $\text{YO}_{1.5}$ content in the TBC reduces the volume of TBC that must react for the crystallized volume to exceed the volume of TBC reacted, and for the melt to be fully crystallized.

coating compositions that maximize the ratio $V_{\text{crys}}/V_{\text{TBC}}$ over the widest range of deposit compositions. Additional benefit is gained in cases where a significant portion of the added volume is derived from phases such as apatite, which nucleate quickly and grow with a favorable morphology for blocking the infiltration channels. In one scenario, phase equilibrium calculations can be used to simulate how the reaction product constitution and residual melt composition evolve as a TBC is progressively consumed through reactions with a fixed amount of deposit. The mechanics of the calculation are similar to those described for EBC systems in the prior Section, but now the physical interpretation corresponds to a fixed volume of melt reacting with the coating within an infiltrated feature in the coating architecture, i.e., increasing X_{TBC} in Fig. 6a.

The capability of this type of calculation is demonstrated for three TBC materials in the $\text{YO}_{1.5}$ - ZrO_2 system in Fig. 7. The first two, 7YSZ and $\text{Y}_4\text{Zr}_3\text{O}_{12}$, are commonly studied TBC materials. The third, containing 80 mol% $\text{YO}_{1.5}$ and denoted $\text{Y}_{80}\text{Zr}_{20}$, corresponds approximately to the high-temperature solubility limit of ZrO_2 in cubic $\text{YO}_{1.5}$ (bixbyite)⁴² and the ordered H_3 phase ($\text{RE}_6\text{ZrO}_{11}$) reported in many $\text{REO}_{1.5}$ - ZrO_2 systems.¹⁰³ It is selected to illustrate the potential benefit of a higher- $\text{YO}_{1.5}$ TBC for CMFAS mitigation. In all three cases, the relative volume of liquid increases initially as the TBC dissolves until saturation is reached. During this nascent period, $V_{\text{crys}}/V_{\text{TBC}}$ is much less than unity for all three coating materials. This ratio initially increases fastest for

7YSZ owing to the lower solubility of ZrO_2 compared with $\text{YO}_{1.5}$ in the silicate melt. The implication is that a 7YSZ coating would experience less dilation of infiltration channels early in the process. However, because the ZrO_2 -based reactive crystallization products are not favored for this deposit composition, the $V_{\text{crys}}/V_{\text{TBC}}$ for 7YSZ increases to asymptote just below unity. Conversely, the higher $\text{YO}_{1.5}$ solubility in the melt implies increased channel dilation in the initial stages of the reaction for $\text{Y}_4\text{Zr}_3\text{O}_{12}$ and $\text{Y}_{80}\text{Zr}_{20}$. The subsequent stabilization of apatite (not shown in Fig. 7, but captured in phase fracture data generated by the calculations) leads to rapid increase in $V_{\text{crys}}/V_{\text{TBC}}$ and reduction in the melt volume. The melt is exhausted sooner, and with a higher final $V_{\text{crys}}/V_{\text{TBC}}$ for $\text{Y}_{80}\text{Zr}_{20}$ owing to the enhanced reactivity associated with the higher $\text{YO}_{1.5}$ content. Coupled with preliminary evidence that increasing the $\text{YO}_{1.5}$ content in the TBC material also increases the dissolution rate,¹⁰² the implication is that the $\text{Y}_{80}\text{Zr}_{20}$ would be more effective at sealing the infiltration channels than a

$\text{Y}_4\text{Zr}_3\text{O}_{12}$ coating. This effect has been confirmed experimentally for analogous $\text{YbO}_{1.5}$ -based coating materials.¹⁰⁴

While the calculation strategy illustrated in Fig. 7 is effective for understanding the reaction behavior for a single (or perhaps several) deposit/TBO combinations, it does not lend itself to rapid comparisons between the behaviors of multiple deposits or TBC material combinations. An alternative approach to screen for transitions in behavior involves performing phase equilibrium calculations covering a range of coating and deposit compositions with each representing a single point in the reaction progression at fixed X_{TBC} . The general strategy for calculations intended to probe the effect of changing the ZrO_2 : $\text{REO}_{1.5}$ ratio in the TBC on the reactivity with a given deposit composition involves a series of phase equilibrium calculations performed for a fixed TBC:deposit ratio for the complete range of ZrO_2 : $\text{REO}_{1.5}$ ratios. The resulting phase fractions can then be graphically presented as a stacked area plot (see Figs. 8 and 9) to show the conditions under which the reactions result in a net increase or decrease in crystalline volume $V_{\text{crys}}/V_{\text{TBC}}$.

To illustrate the potential utility of this modeling strategy, example calculations were carried out to compare the response of changes in the ZrO_2 : $\text{REO}_{1.5}$ ratio for $\text{GdO}_{1.5}$ - vs $\text{YO}_{1.5}$ -containing zirconate coatings when exposed to three representative deposit compositions at 1300 °C and 1400 °C. The results comparing the reactions with a $\text{C}_{31}\text{M}_9\text{F}_5\text{A}_{12}\text{S}_{43}$ deposit as a function of increasing X_{TBC} for the $\text{GdO}_{1.5}$ - and $\text{YO}_{1.5}$ -based system are shown in Fig. 8a–d and e–h, respectively. In these plots, the liquid (i.e., the initial deposit) is shown in yellow, the reactive crystallization products are shown in purple, and the reprecipitated phases in red, and the intrinsic crystallization products in blue. The approximate value of the V_{TBC}^{**} is shown with a dashed horizontal line in each panel, while V_{crys} is represented by the boundary between the liquid (yellow) and crystalline (red, purple, and blue) phases.

The first striking observation in Fig. 8 is that the $\text{GdO}_{1.5}$ -based systems begin to form apatite at a significantly lower $\text{REO}_{1.5}$ content, and with significantly less TBC dissolution (lower X_{TBC}) than the $\text{YO}_{1.5}$ systems. Thus, the $V_{\text{crys}}/V_{\text{TBO}}$ is higher for a given $\text{GdO}_{1.5}$ vs $\text{YO}_{1.5}$ concentration in the coating. The implication is that in order to achieve equivalent performance, the $\text{YO}_{1.5}$ concentration in a $\text{YO}_{1.5}$ - ZrO_2 coating would need to be significantly higher than the $\text{GdO}_{1.5}$ concentration in a $\text{GdO}_{1.5}$ - ZrO_2 coating. This is consistent with experimental results showing that $\text{Gd}_2\text{Zr}_2\text{O}_7$ coatings are

Fig. 8. Stacked phase fraction plots illustrating changes in the predicted reactivity between a $\text{C}_{31}\text{M}_9\text{F}_5\text{A}_{12}\text{S}_{43}$ deposit and thermal barrier oxides in the (a–d) $\text{GdO}_{1.5}$ - ZrO_2 and (e–h) $\text{YO}_{1.5}$ - ZrO_2 systems at 1300 °C. The calculations capture the effects of changes in the $\text{Zr}:\text{RE}$ content in the coating (abscissa in each panel) and the relative molar fraction of TBC reacted with the deposit (X_{TBC} , increasing from top to bottom). The horizontal line represents approximately V_{TBC} .

**Here the molar volumes for the relevant oxides are within a few percent of one another on the basis of gram atoms of cations for single cation formulae, so the mole fractions can be used interchangeably for volumes without significantly changing the interpretation.

Fig. 9. Stacked phase fraction plots illustrating the effect of changing temperature (a vs b) and deposit composition (b, c, d) on the reactivity of TBCs in the $\text{YO}_{1.5}$ - ZrO_2 system with silicate deposits at $X_{\text{TBC}} = 0.25$.

generally more resistant to infiltration than $\text{Y}_4\text{Zr}_3\text{O}_{12}$ with a similar CMAS composition at 1300°C , even though the latter coating contains a higher $\text{REO}_{1.5}$ fraction.² It is also notable that for a range of coating compositions around 30 mol% $\text{YO}_{1.5}$, $V_{\text{cryst}}/V_{\text{TBO}}$ remains significantly below unity even with a relatively high dissolved X_{TBC} . At the same time, coatings with a higher $\text{REO}_{1.5}$ concentration see a marked increase in $V_{\text{cryst}}/V_{\text{TBO}}$ (to the point that the melt is nearly eliminated) due to the onset of intrinsic crystallization alongside apatite crystallization.

Figure 9 illustrates the effect of changing temperature and deposit composition on the deposit reactivity of the $\text{YO}_{1.5}$ -containing TBC materials. This analysis uses $\text{C}_{31}\text{M}_9\text{F}_5\text{A}_{12}\text{S}_{43}$ at 1300°C and with $X_{\text{TBC}} = 0.25$ as an anchor [shown in Fig. 8h and again in Fig. 9b]. It is observed that increasing the temperature from 1300 to 1400°C [cf. Fig. 9a and b] results in modest reduction in the fractions of fluorite and apatite formed, owing to increased $\text{YO}_{1.5}$ solubility in the melt, while the melilite expected to form with higher- $\text{YO}_{1.5}$ materials is no longer stable. The effect of increasing the SiO_2 concentration in the deposit is illustrated by moving left to right in Fig. 9b, c and d. The notable change is the stabilization of zircon as an additional reactive crystallization product. For $\text{C}_{20}\text{M}_5\text{F}_5\text{A}_{10}\text{S}_{60}$ (with intermediate SiO_2 content), the $\text{YO}_{1.5}$ -lean compositions produce a mixture of zircon and $t\text{-ZrO}_2$. In $\text{C}_{10}\text{M}_5\text{F}_5\text{A}_{10}\text{S}_{70}$, with the highest SiO_2 content, all of the ZrO_2 is converted to zircon. Interestingly, at this point in the reaction progression, the capacity to form apatite does not change significantly as a function of the Ca:Si ratio in the deposit since the consumption of SiO_2 in zircon acts to buffer the Ca:Si ratio. The results of such calculations could be further simplified in terms of the overall $V_{\text{cryst}}/V_{\text{TBO}}$ for each condition investigated to facilitate direct overlay for visualization.

OUTLOOK

This article describes recent progress in the development and application of thermodynamics models to understand deposit-induced degradation of advanced coatings in turbine engines. It also illustrates the power of these modeling approaches to predict coating behavior and to accelerate the design of new coating materials and architectures. Ongoing research to expand the databases underpinning these models is important to enable their application to a wider range of coating compositions. There is also a critical role for complementary modeling approaches to capture the dynamic effects of coating infiltration and reaction, as well as the ensuing thermomechanical effects that dictate coating durability.

The examples provided herein focused on coatings based on yttrium silicates and zirconates and gadolinium zirconates because presently the thermodynamics descriptions of these systems are the most robust. However, there is interest in a variety of other TBC and EBC materials owing to other properties of interest. For instance, ytterbium disilicate is preferred to yttrium disilicate for EBC applications owing to undesirable polymorphic transitions during processing in the latter. There has also been interest to develop EBCs based on $\text{REO}_{1.5}$ - TiO_2 systems,¹⁰⁵ and TBCs containing TiO_2 and $\text{TaO}_{2.5}$.^{106–109} While there have been some experimental studies to assess how each of these novel coating candidates reacts with CMFAS-type deposits,^{22,105,108} the lack of thermodynamic models for the relevant Yb-, Ta-, and Ti-oxide subsystems complicates the implementation of models for these systems. There is a need to further basic scientific investigations to determine the key phase relationships and thermodynamic properties necessary to enable future extensions of the thermodynamic databases to encompass these systems.

Furthermore, despite the capabilities of the modeling approaches described here, for a complete description of the coating performance it is also important for models to capture the infiltration dynamics, rates of coating dissolution and reprecipitation, and the microstructure of the reaction product layers. In some cases, physics-based models of these processes exist and can be used with minimal additional experimental input. In other cases, significant experimental data is needed to capture temperature- and deposit composition-dependent kinetic parameters. Rather than making the investment to collect this detailed data for each coating system of interest, there may be benefits in applying non-physics-based machine learning models fed with a combination of sparse experimental data that already exists for common coating systems and computational features based on thermodynamics and thermophysical property models.

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CONFLICT OF INTEREST

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