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14. ABSTRACT

This project aimed to develop the scientific foundation for TBC concepts that are sufficiently robust to withstand CMAS degradation in current and future gas turbine engines with expected material temperatures ≥1300°C. The overarching goal was to elucidate the dynamics of the infiltration-dissolution-crystallization processes that eventually arrest the CMAS penetration into the TBC, and to assess the robustness of the affected TBC system under static and changing thermal gradients. The approach involved three distinct activities: (i) characterizing and understanding CMAS related damage mechanisms in field specimens provided by industrial collaborators, (ii) investigating the reaction kinetics of different CMAS and CMAS/TBC combinations using differential scanning calorimetry and isothermal furnace exposures, and (iii) evaluating the thermomechanical response of infiltrated systems to varying thermal gradients using a laser based test facility developed at UCSB under this project. Modeling aspects were addressed through collaborations with other investigators. The overarching themes were microstructure evolution, its connection to material and environmental parameters, and its thermo-mechanical implications. The expected benefit to the US Navy would be (i) a science-based strategy to guide coating design for CMAS environments through suitable control of the composition and architecture, (ii) an enhanced scientific foundation for high temperature materials and (iii) the training and diversity of human resources in this important area.

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SCIENCE UNDERPINNING TBC DESIGN TO OVERCOME THE CMAS THREAT TO PROGRESS IN GAS TURBINE TECHNOLOGY

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Abstract

This project aimed to develop the scientific foundation for TBC concepts that are sufficiently robust to withstand CMAS degradation in current and future gas turbine engines with expected material temperatures ≥1300°C. The overarching goal was to elucidate the dynamics of the infiltration-dissolution-crystallization processes that eventually arrest the CMAS penetration into the TBC, and to assess the robustness of the affected TBC system under static and changing thermal gradients. The approach involved three distinct activities: (i) characterizing and understanding CMAS related damage mechanisms in field specimens provided by industrial collaborators, (ii) investigating the reaction kinetics of different CMAS and CMAS/TBC combinations using differential scanning calorimetry and isothermal furnace exposures, and (iii) evaluating the thermomechanical response of infiltrated systems to varying thermal gradients using a laser-based test facility developed at UCSB under this project. Modeling aspects were addressed through collaborations with other investigators. The overarching themes were microstructure evolution, its connection to material and environmental parameters, and its thermo-mechanical implications. The expected benefit to the US Navy would be (i) a science-based strategy to guide coating design for CMAS environments through suitable control of the composition and architecture, (ii) an enhanced scientific foundation for high temperature materials and (iii) the training and diversity of human resources in this important area.

Progress Statement

Substantial progress was made in all fronts, as described in the various annual reports and summarized below. Improved understanding of the CMAS-related damage mechanisms was achieved, with emphasis on those forms of damage related to melt penetration and thermo-chemical interactions, but also on the feasibility of TGO damage by vapor-assisted transport of oxides through the TBC, the latter through collaboration with Honeywell Aerospace. Additional insight emerged from analysis of the melting and crystallization behavior of model silicate compositions by comparison of DSC experiments with calculations of viscosity and melt fragility parameters based on a literature model. The dissolution-reprecipitation mechanism was clearly demonstrated in glass beads containing small amounts of thermal barrier oxides. These studies are continuing under the renewed grant, focusing on assessing the dissolution and reprecipitation kinetics. Substantial insight emerged from adapting and applying the LayerSlayer model to assess the stresses and energy release rates in multilayer systems with CMAS penetration into the thermal barrier layer. Of particular interest was the difference in behavior between rapid transients and slow cooling conditions. The relevance of the CMAS viscosity and crystallization kinetics on the depth of penetration was demonstrated using laser gradient tests on 7YSZ coatings and two CMAS with different compositions. Of particular significance was the role of Fe in enabling crystallization to occur under a thermal gradient and arrest CMAS penetration. The role of TBC microstructure in the sensitivity to CMAS mitigation was examined using a Sm zirconate coating deposited by DVD, in collaboration with H.N.G. Wadley's ONR project. Preliminary models were developed and used to guide the design of experiments to generate stresses in the bond coat that can lead to creep cavitation. The first experiments provided significant insight on the evolution of buckling and spallation events under thermal cycling representative of what may occur in actual engine operation. Finite element models are being developed under the renewed grant, in collaboration with M.R. Begley's ONR project, to analyze this test and additional experiments are ongoing to identify the conditions conducive to void formation. An experimental set up for testing of CMAS-penetrated TBC-coated specimens subject to both mechanical load and thermal cycling has been designed and will be finalized and tested under the renewed grant.

Technical Objectives

This research program aimed to develop the scientific foundation for TBC design concepts that are sufficiently robust to withstand degradation by calcium-magnesium-alumino-silicate (CMAS) deposits under the higher temperatures expected in advanced gas turbines. Prior work revealed that CMAS penetration within the pore network of TBCs is arrested at a depth dictated by the rate of the capillary-driven flow, the crystallization kinetics of CMAS and the imposed thermal gradient [1-3]. Mitigation strategies are generally based on dynamically modifying the composition of the inward flowing CMAS by dissolution of the TBC or a suitable sacrificial oxide to induce crystallization as close to the surface as possible [1,4] (Figure 1). An overarching goal was to understand the relationships between temperature, crystallization kinetics and CMAS composition, especially as modified by dissolution of thermal barrier oxides, and the synergism with capillary flow into a decreasing temperature gradient. Arguably, if the optimum constitution of the reaction products were understood, one could precondition the surface by creating a thermodynamically and/or kinetically stable barrier layer prior to service. However, the optimal solution is likely to depend on the chemistry of the silicate deposit, which can be quite variable [1,5].

Fig. 1. Multilayer thermal barrier system with reactive outer layer that minimizes CMAS penetration.

Technical Approach

The project comprised three broad activities. The first one focused on identifying and understanding the failure mechanisms in engine components affected by CMAS deposition. Much of the effort in this area has been on the microstructural and microchemical characterization of selected field specimens provided by the OEMs. This activity identified three distinct forms of damage ascribed to CMAS penetration of the TBC, Fig. 2. The goal of the second activity was to understand the thermochemical interactions between CMAS and current/prospective thermal barrier oxides, and the manner in which these chemical in-

Fig. 2. Expanded menu of CMAS related failure mechanisms, wherein the delamination cracks can propagate (i) through the TBC, either by shallow or deep delaminations, (ii) through the TGO when the latter is chemically attacked by the CMAS, or (iii) through the bond coat by nucleation, coalescence and linkage of creep cavities into cracks.

teractions may lead to mitigation strategies. In general, that involves forming a layer of reaction products that separates the CMAS melt on the surface from the open porosity in the TBC. A key feature is an increased emphasis on the dependence of the reaction on the CMAS composition, both in terms of the relative proportion of the key constituents, notably the ratio of modifiers to glass formers in the melt, as well as the role of other oxides commonly found in the deposits, notably those of Fe and Ti. (The PI was also involved in a Phase II STTR with QuesTek Innovations, funded by ONR, aimed at developing a thermodynamic database for multicomponent oxides relevant to CMAS-TBC interactions.) Because in all cases there is a stiffened layer formed on top of the TBC, the third core activity addresses the thermo-mechanical response of that layer to different thermal scenarios. A laser gradient test facility developed earlier in this project continues to be improved, most recently with the addition of a higher resolution pyrometer.
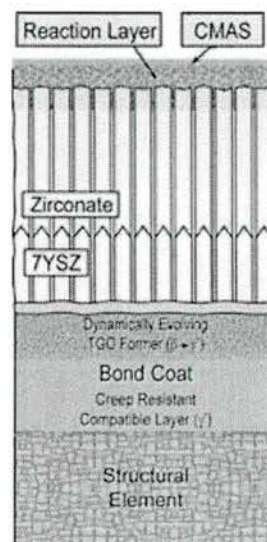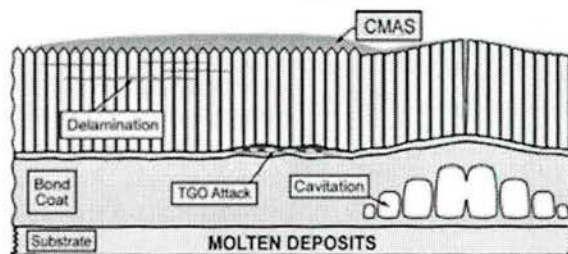
Summary of Technical Accomplishments

Research under ONR sponsorship established the foundation for understanding the mechanisms of penetration of silicate melts into TBCs, with emphasis on the thermochemical interaction between CMAS and the state-of-the-art 8YSZ TBC [5,6], as well as the thermomechanical damage ensuing from it [2,3]. A mitigation strategy based on the reaction of CMAS with pyrochlore or δ-phase zirconates has been extensively investigated [1,4,7-9]. Engine evidence has shown that $Gd_2Zr_2O_7$ (GZO), originally introduced for its low-k, performed remarkably better than conventional YSZ in CMAS environments [1,10]. Mechanisms identified under ONR research have proven to be operational in field specimens [11], but concerns about the low toughness of this material [9,12] still persist. Research has focused on three major topics, related to the dynamics of infiltration of the silicate melt into the TBC and its consequences on the thermomechanical behavior. A brief summary is provided below.

Crystallization dynamics.

This was the main focus of Zaleski's dissertation [7] and a very important element of Poerschke's dissertation [13]. The overarching goal was to understand the intrinsic crystallization kinetics of CMAS and how it is modified by the interaction with TBCs, as relevant to the development of a mitigation strategy. Salient outcomes and implications are described below.

- Baseline CAS compositions exhibit reasonably consistent melting behavior in differential scanning calorimetry (DSC), but at temperatures lower than those expected from the phase diagram [5]. This highlights the implications of non-equilibrium combinations of minerals depositing on the coating, even if the nominal oxide concentrations are comparable.

- Higher alumina contents promote crystallization of CAS melts, ascribed to the increased tendency to form anorthite. Mg additions to CAS elevate the onset of melting but do not seem to have a strong effect on crystallization. Conversely, Fe promoted crystallization in the compositions investigated. The effects of Mg could be rationalized on the basis of the phase equilibria and estimated viscosities and melt fragilities, but not the effects of Fe [5].
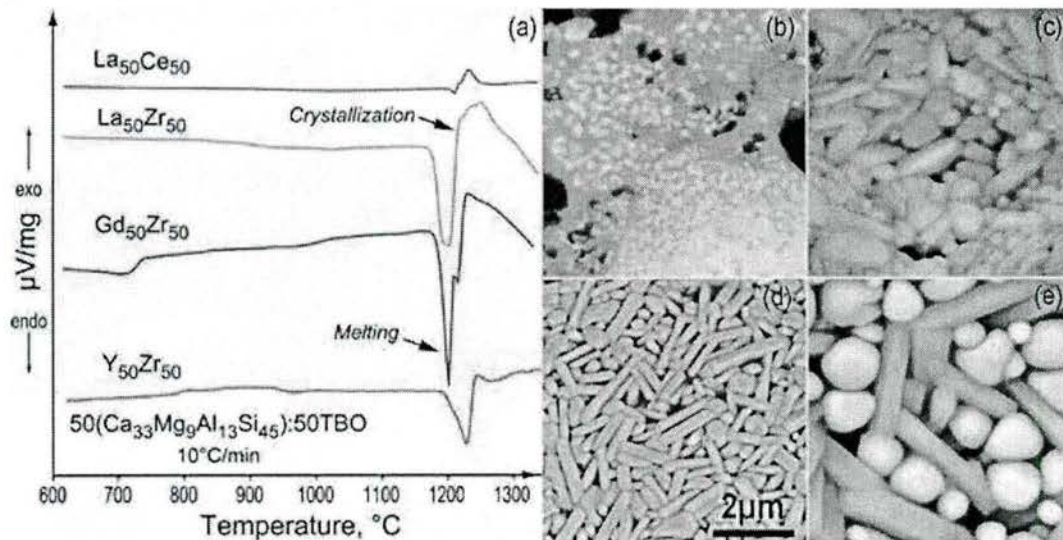

Fig. 3. (a) DSC scans of the melting of mixtures of CMAS with different rare earth compounds. The micrographs correspond to the reaction products between CMAS and (b) $La_2Ce_2O_7$ (fluorite), (c) $La_2Zr_2O_7$ (pyrochlore), (d) $Gd_2Zr_2O_7$ (pyrochlore) and (e) $Y_2Zr_2O_7$ (fluorite + δ-phase). The elongated particles are apatite and the globular ones fluorite. In all cases there is little glass left after the reaction.

- DSC of CMAS+8YSZ revealed no significant effect on the thermal response, except for a modest depression of the onset of melting, while microstructural evidence showed extensive dissolution and re-precipitation. The same experiments on oxides active in mitigating penetration, specifically GZO, exhibited a distinct exotherm associated with the crystallization of apatite, Fig. 3(a) [7]. The strength of that exotherm was related to the Gd concentration in ZrO_2 and the extent of apatite formation, which suggested a path to assess the effectiveness of mitigating oxides. However, experiments in other materials revealed that the melting endotherm and crystallization exotherm interact to different degrees depending on the crystallization kinetics, as illustrated in Fig. 3(a), requiring additional insight. Microstructural analysis confirmed that in all cases the melt is largely consumed in the formation of apatite, with the excess ZrO_2 forming globular fluorite particles, e.g. Fig. 3(e).

Results from the DSC studies provided guidance for isothermal exposures of coatings to CMAS, as well as for thermal gradient experiments discussed later. They also highlighted the importance of understanding the dissolution process, and the interplay between viscosity and the melting/crystallization behavior. These issues are being investigated in the renewed grant.

Research under this grant also expanded the understanding of the roles of temperature and chemical composition of the REZ/REH on the nature of the crystallization products and the potential for mitigation [8]. Figure 4 summarizes the compositions of the fluorite and apatite phases produced by reaction of $Ca_{33}Mg_9Al_{13}Si_{45}$, a composition used for prior studies in this project, with REZs and REHs of different cation sizes, ranging from Yb to La. It is first noted that the apatite formed in all cases had a nearly constant Ca:RE ratio, ~1/4 (Fig. 4b) regardless of temperature. This is at variance with other reports that smaller RE cations promote the formation of apatites with Ca:RE~2:3 [14]. Apatite silicates with the higher Ca:RE ratio do exist [15], but the current results suggest that when formed from silicate melts the crystallization product with the lower Ca:RE ratio is favored. The issue is relevant to the RE efficacy in capturing SiO_2 and is under investigation in the renewed grant.

A more significant implication is the large variation in the reprecipitated fluorite composition shown in Fig. 4(a). As the RE cation radius decreases the amount of RE recaptured by the fluorite upon reprecipitation increases. The inference is that for the smaller cations more of the TBC would have to be dissolved to form enough apatite to block the channels in the microstructure. From this perspective La compounds appear more effective, but they present more challenges in processing.

Isothermal and laser gradient experiments in Yb-based coating systems have shown that $Yb_4Zr_3O_{12}$ and $Yb_4Hf_3O_{12}$ do not provide adequate protection even at 1300°C [16], as inferred from Fig. 4(a).
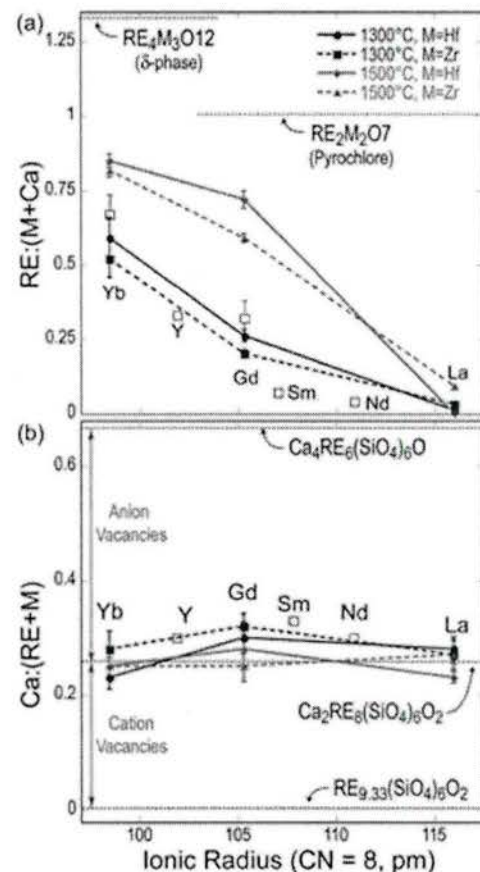

Fig. 4. Composition of the (a) fluorite and (b) apatite crystallization products of the reaction between $C_{33}M_9A_{13}Si_{45}$ and RE zirconates/hafnates, in pellet and/or EBPVD coatings, at 1300°C and 1500°C.

Moreover, $Gd_2Zr_2O_7$ (GZO) coatings, which have proven effective for CMAS mitigation at temperatures in the range 1200-1300°C, are susceptible to penetration at 1500°C, the target temperature for EBC/CMC systems [13]. It is hypothesized that the primary problem results from the substantial reduction in viscosity and the concomitant increase in the infiltration rate as the temperature increases, which results in a reduced time available for the dissolution/reprecipitation reaction to generate crystalline phases that can block the flow paths into the coating. Increasing the rare earth concentration or alloying with a more active cation, e.g. Yb+La, may provide a path for improving performance, further motivating the need for understanding of the various components of the infiltration dynamics and their dependence on coating and CMAS composition.

Bond coat cavitation.

This investigation has been undertaken in close collaboration with GE Aviation. It is the topic of Kaylan Wessels dissertation, to be completed in June 2016, and involves laser gradient test (LGT) experiments with R.W. Jackson, discussed later. Extensive microstructural analysis has been undertaken on several airfoils from two different engines. A key finding is that the TBCs are heavily impregnated with CMAS, in some cases through the entire thickness (Fig. 5b). However, the delamination does not occur through the TBC or even along the TGO, but rather by the evolution and linkage of cavities within the bond coat, presumably by cyclic creep. The observations suggest there are two populations of cavities: (i) smaller ones nucleated at embedded grit particles, which eventually evolve into crack-like voids, and (ii) larger globular cavities that appear to initiate at the bond coat/TGO interface.
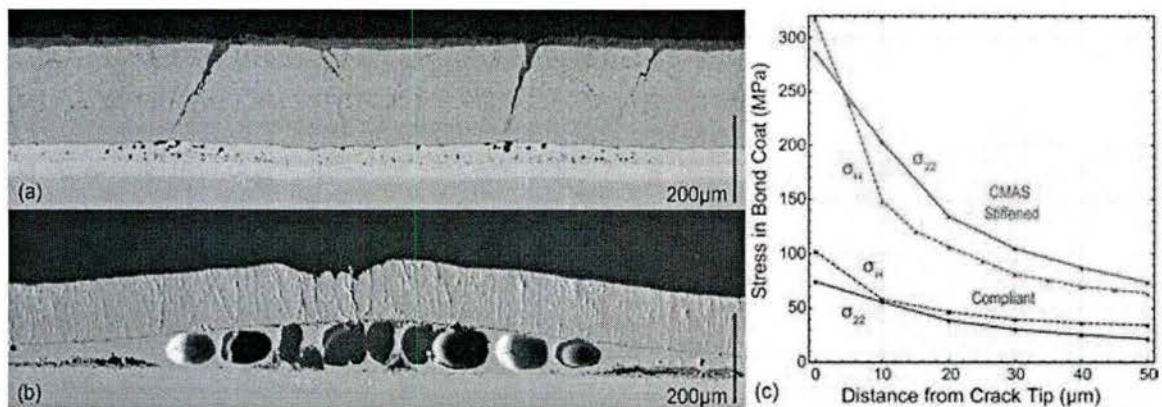
Fig. 5. Bond coat cavitation in airfoils with CMAS-impregnated TBCs and examples of possible stress scenarios. The thicker coating (a) is initially penetrated half way, whereas the thinner coating (b) is fully penetrated. The graph in (c) depicts the calculated hydrostatic (σ_H) and out of plane (σ_{22}) components of the stress within the bond coat arising from a through thickness crack in the TBC under an in-plane stress in the substrate. Note the difference in stresses between a compliant coating (no CMAS) and one stiffened by CMAS infiltration. (Specimens courtesy of GE Aviation.)

In one scenario, depicted in Fig. 5(a), clusters of cavities appear to evolve below cracks traversing the coating thickness. Stresses generated within the bond coat as a result of a crack of this type have been calculated using a simplified finite element model. The results are depicted in Fig. 5(c), which shows the critical effect of the CMAS penetration on the magnitude of the stress. As expected, the higher stresses are closer to the TGO interface and decay with distance into the coating. However, nucleation is more likely at embedded particles, which concentrate at the "grit line". These initial calculations suggest a scenario that could give rise to cavities both at the TGO interface as well as at the boundary with the interdiffusion zone. However,

they do not yet explain the severe cavitation observed in Fig. 5(b), which does not appear to involve any coating cracks.

Characterization of field specimens and analysis of different stress scenarios that could explain the failure mechanism will be continued in the reminder of the current funding period, and should be completed during the first year of the proposed project. A parallel effort, described below, attempts to use the understanding emerging from the models and observations to replicate the mechanism in a laboratory setting.
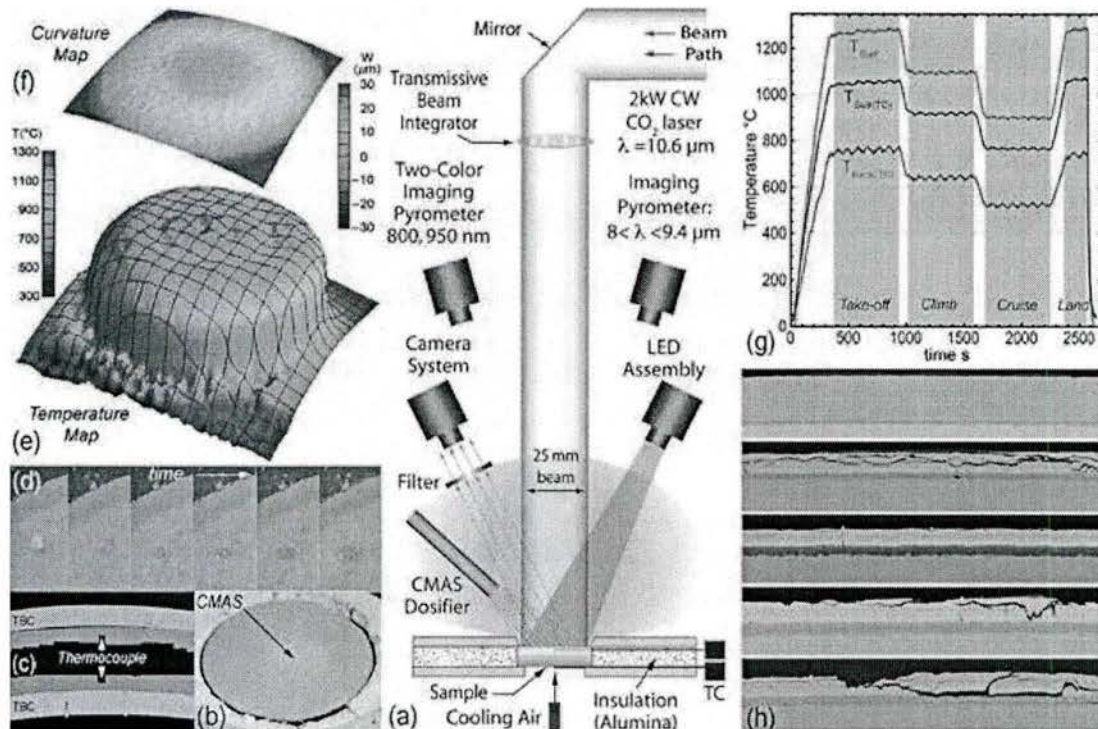

Fig. 6. Laser Gradient Test facility at UCSB. (a) Schematic of the experimental set up with thermocouples to measure the temperature at the bottom of the specimen, cooled by compressed air, and that under the TGO. (b) Coupon with CMAS deposit. (c) Capabilities for testing samples with curved surfaces. (d) Progression of a melting CMAS particle landing on the coating, using the blue LED illumination and camera system. (e) Surface temperature profile from high resolution imaging pyrometer. (f) Curvature of sample corresponding to the profile in (e), measured by DIC. (g) Capability for complex cycles simulating engine exposure (guidelines from PWA), (h) Cross sections of coatings showing different modes and degrees of damage depending on top coat, substrate CTE mismatch and cooling rates.

Mechanistic studies under thermal gradients.

A major asset for investigating the mechanisms associated with CMAS penetration, damage, and potential mitigation is a laser gradient test (LGT) facility developed at UCSB over the past few years, supported substantially by ONR funding. The facility and its capabilities, illustrated in Fig. 6, is based on a continuous 2kW CO_2 laser with optics that provide nearly constant illumination over the entire specimen (Figs. 6a,e). Coupons are typically 25 mm in diameter and may be nominally flat (Fig. 6b) or have curved surfaces mimicking the profiles of the pressure and suction sides in an airfoil (Fig. 6c). The facility has been enhanced with a state-of-the-art imaging pyrometer and digital image correlation (DIC) capabilities at high temperature [17] over the

past period, allowing measurements of distortions that can help validate improved mechanics models.

During the current funding period there has been a concerted effort to improve the earlier mechanics models for CMAS penetrated TBCs [18] through collaborations with J.W. Hutchinson [1] and especially with M.R. Begley (UCSB) [19]. Begley has developed a suite of software tools for multilayer architectures under stress, known as LayerSlayer™ [20], which have been adapted in this project to plan and analyze the LGT experiments of CMAS on TBCs [3]. Salient accomplishments include:

- The demonstration that complex thermal cycles representative of what may be expected in an engine can be produced with the laser set up in Fig. 6. This capability, coupled with knowledge of the material properties, has been used to design and test cycles that may create scenarios responsible for the creep cavitation phenomena in Fig. 5. While coating buckling, cracking and delamination damage have been produced, all the failure modes have been through the CMAS-impregnated TBC or along the TGO, and not through the bond coat. The behavior was ascribed to the model CMAS composition utilized, which penetrates and attacks the TGO before stresses sufficiently high to generate cavities can develop in the bond coat. Such attack is not observed in the hardware, suggesting the need for understanding the role of CMAS composition in the process, motivating one of the activities being supported under the renewed project.

- A study of the effects of cooling rate, thermal expansion mismatch between substrate and coating, and CMAS loading on the propensity to form delamination cracks in GZO coatings (see illustrations in Fig. 6h, where the top image corresponds to 8YSZ and the rest to GZO coatings). The responses have been qualitatively consistent with the variations in energy released rate produced by the multilayer mechanics analysis, but no scenario precluding thermomechanical damage in the coating has been produced in practice, at variance with engine experience [10]. *This highlights the need to better understand the experiment and identify the parameters that mark the boundaries of the "fail safe" regime.*
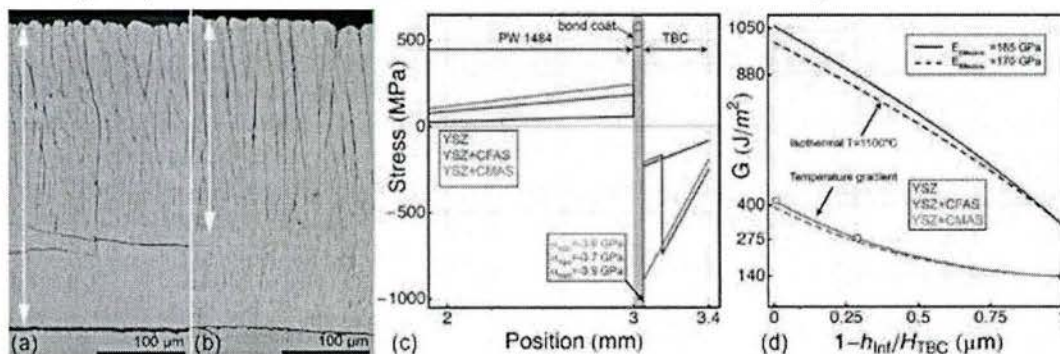

Fig. 7. Illustration of the role of the silicate deposit composition on the penetration of two comparable 8YSZ TBCs supplied by PWA. The substrate is PWA1484, with a 30μm thick NiCoCrAlY bond coat and a 300μm EB-PVD top-coat. The silicate deposits and corresponding melting ranges determined by DSC were (a) $C_{33}M_9A_{13}S_{45}$ (1233-1260°C), and (b) $C_{13}Fe_{10}A_{18}S_{59}$ (1101-1158°C). Both specimens were subjected to 5 cycles in a LGT with a surface temperature of ~1300°C, a TGO temperature of ~1000°C and a backside temperature of ~850°C. The arrows in (a) and (b) indicate the depth of CMAS penetration, established in the first cycle. The stress distributions after cooling for non-infiltrated YSZ as well as YSZ infiltrated with CMAS and CFAS are shown in (c), and the energy release rates in (d). Note in (d) that comparable isothermal exposures would lead to higher ERR than exposure in a thermal gradient.

- Notwithstanding the ability to induce very large thermal gradients through the TBC, experiments with $C_{33}M_9A_{13}S_{45}$ led to complete penetration of EBPVD TBCs based on 8YSZ (Fig. 7a), at variance with observations on hardware [6,21]. Examination of the channels closer to the TGO reveals the CMAS to be amorphous [3], whereas hardware tends to show crystalline CMAS at the bottom of the penetrated layers. Preliminary experiments with $C_{13}Fe_{10}A_{18}S_{59}$ show arrest of penetration at ~2/3 of the thickness (Fig. 7b). Estimates of the stresses and energy release rates (Fig. 7c) show that the higher penetration for CMAS results in a ~50% increase in the driving force for delamination relative to CFAS. Model calculations suggest that the latter composition has higher viscosity than the former, while DSC reveals a stronger tendency to crystallization at higher temperatures. The characteristics of the CMAS are thus important in understanding the extent of penetration and the mechanical response, motivating activities being pursued in the renewed project.

Contribution to Human Resources and Dissemination.

Two students received Ph.D.s acknowledging support from grant N00014-08-1-0522 during this period. Elisa M. Zaleski, who graduated in January 2013 and immediately joined the Pratt &Whitney Aircraft Coatings group in East Hartford, CT. David L. Poerschke, who was supported earlier by an NDSEG fellowship, preformed his research initially under a related ONR grant (0322) and a related AFOSR STTR, and finished under this grant (0522). He graduated in February 2014 and is now as a post-doctoral research in an ONR STTR with QuesTek innovations at UCSB. Dr. Poerschke is effectively functioning as a co-PI in the QuesTek project as well as in a CMC project sponsored by NASA. He is currently looking for a faculty position. A postdoctoral researcher, Dr. R. Wesley Jackson, has been supported part time by this project and has worked closely with Prof. Begley on the LayerSlayer™ improvements. He is currently considering offers from various companies.

During this time, the PI has played a leading role in the international community researching CMAS effects on coatings, as chair of two focused workshops on High Temperature Coatings at UCSB in 2012 and 2014, and currently as co-chair of the ECI Thermal Barrier Coatings IV conference, held in Irsee, Germany, June 22-27, 2014. Since 2011 the PI has given over 30 invited talks involving, at least in part, results from this project, and the students involved have given talks at ICMCTF, MS&T, TMS, ICACC and GE Research. The PI was named Fellow of the American Ceramic Society in 2012 and received the 2014 TMS Morris Cohen Award.

Publications acknowledging funding under this grant.

1. D. L. Poerschke, G. G. E. Seward, and C. G. Levi, "Influence of Yb:Hf Ratio on Ytterbium Hafnate/Molten Silicate (CMAS) Reactivity¶," *Journal of the American Ceramic Society,* (in press, published online October 2015).

2. T. R. Kakuda, C. G. Levi, and T. D. Bennett, "The thermal behavior of CMAS-infiltrated thermal barrier coatings," *Surface and Coatings Technology,* **272** 350-356, (2015).

3. R. W. Jackson, E. M. Zaleski, D. L. Poerschke, B. T. Hazel, M. R. Begley, and C. G. Levi, "Interaction of Molten Silicates with Thermal Barrier Coatings under Temperature Gradients.," *Acta Materialia,* **89** 396-407, (2015).

4. E. M. Zaleski, C. Ensslen, and C. G. Levi, "Melting and Crystallization of Silicate Systems Relevant to Thermal Barrier Coating Damage," *Journal of the American Ceramic Society,* **98** [5] 1642-1649, (2015).

5. "Effect of cation substitution and temperature on the interaction between thermal barrier oxides and molten CMAS," David L. Poerschke and Carlos G. Levi, Journal of the European Ceramic Society 35 (2015) 681-691.

6. D. L. Poerschke, D. D. Hass, S. Eustis, G. G. E. Seward, J. S. Van Sluytman, and C. G. Levi, "Stability and CMAS resistance of Ytterbium-silicate/hafnate TBC/EBCs for SiC Composites," *Journal of the American Ceramic Society,* **98** [1] 278-286, (2015).

7. A. G. Evans, D. R. Clarke, and C. G. Levi, "Turbine Materials and Mechanics." Ch. 12 in *Turbine Aerodynamics, Heat Transfer, Materials and Mechanics,* Edited by T. I.-P. Shih and V. Yang. **Vol. 243**. in Progress in Astronautics and Aeronautics, Series Ed. T. C, Lieuwen, The American Institute of Aeronautics and Astronautics (AIAA), (2014).

8. H. B. Zhao, C. G. Levi, and H. N. G. Wadley, "Molten Silicate Interactions with Thermal Barrier Coatings," *Surface and Coatings Technology,* **251** 74-86, (2014).

9. C. G. Levi, J. W. Hutchinson, M.-H. Vidal-Setif, and C. A. Johnson, "Environmental Degradation of TBCs by Molten Deposits," *MRS Bulletin,* **37** [10] 932-941, (2012).

10. H. B. Zhao, C. G. Levi, and H. N. G. Wadley, "Vapor deposited samarium zirconate thermal barrier coatings," *Surface and Coatings Technology,* **203** [20-21] 3157-3167, (2009).

Broader Impacts

The work funded under this program has contributed to the understanding of the degradation mechanisms for state-of-the-art TBC materials and has identified viable solutions to mitigate these mechanisms. The research has set the foundation for an ICME-type framework to guide the design of CMAS resistant TBCs, which is being pursued under the renewal grant and collaborations with other ONR programs as well as industrial and academic organizations. It is anticipated that this effort will lead to the development of a fundamental, mechanism-based infrastructure to overcome the CMAS related barriers to progress in propulsion technology of interest to the Navy, the other DOD services and commercial aircraft.

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1. C. G. Levi, J. W. Hutchinson, M.-H. Vidal-Setif, and C. A. Johnson, "Environmental Degradation of TBCs by Molten Deposits," *MRS Bulletin,* **37** [10] 932-941, (2012).

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