

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

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1. REPORT DATE (DD-MM-YYYY) 29-08-2010		2. REPORT TYPE Final		3. DATES COVERED (From - To) 01/01/07 - 05/31/10	
4. TITLE AND SUBTITLE High Temperature Evolution of PtNiAl-Based Thermal Barrier Coatings From First Principles Simulations				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER FA9550-07-1-0063	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S) Emily A. Carter				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Princeton University, Dept. of Mechanical & Aerospace Engineering, Equad, Suite D404a, Princeton, NJ 08544-5263				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) Air Force Office of Scientific Research 875 N. Randolph St. Room 3112 Arlington, VA 22203				10. SPONSOR/MONITOR'S ACRONYM(S)	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S) <i>AFRL AFOSR-VA-TR-2016-0674</i>	
12. DISTRIBUTION / AVAILABILITY STATEMENT Approved for public release; distribution unlimited.					
13. SUPPLEMENTARY NOTES					
14. ABSTRACT This grant was the last in a series to the PI to finish a sequence of thorough investigations via first principles quantum mechanics simulations into atomic scale mechanisms by which jet turbine engine thermal barrier coatings (TBCs) fail, which led to fundamental discoveries as to how and why certain additives (Hf, Y, Pt, etc.) in the coatings help extend their service lifetimes, and ultimately to suggestions for how to improve these high temperature coatings that protect jet turbine engine components. The executive summary focuses on these findings. As the research on TBCs wound down during the last year of the grant, the PI ramped up a new area of research, in solar energy conversion materials. That new research program is just getting started, however, with no publications as yet, and as such is premature to summarize beyond stating that extensive testing of methods to calculate excited states and conduction/valence band edges in transition metal oxides have been carried out, along with preliminary electron/hole mobility studies.					
15. SUBJECT TERMS Thermal barrier coatings, alumina, NiAl, diffusion, grain boundary sliding, hafnium, yttrium, platinum, oxide growth, density functional theory					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT unclassified	b. ABSTRACT unclassified	c. THIS PAGE unclassified			Michael R. Berman
				19	19b. TELEPHONE NUMBER (include area code) (703) 696-7781

Final Report
to
the Air Force Office of Scientific Research
by
Emily A. Carter

Department of Mechanical and Aerospace Engineering and Program in Applied and
Computational Mathematics, Princeton University, Princeton NJ, 08544-5263

Contract/Grant Title: High Temperature Evolution of PtNiAl-Based Thermal Barrier Coatings
from First Principles Simulations

Contract/Grant #: FA9550-07-1-0063

Reporting Period: 1 January 2007 to 31 May 2010

Report Date: August 29, 2010

Executive Summary

This grant was the last in a series to the PI to finish a sequence of thorough investigations via first principles quantum mechanics simulations into atomic scale mechanisms by which jet turbine engine thermal barrier coatings (TBCs) fail, which led to fundamental discoveries as to how and why certain additives (Hf, Y, Pt, etc.) in the coatings help extend their service lifetimes, and ultimately to suggestions for how to improve these high temperature coatings that protect jet turbine engine components. The executive summary focuses on these findings.

As the research on TBCs wound down during the last year of the grant, the PI ramped up a new area of research, in solar energy conversion materials. That new research program is just getting started, however, with no publications as yet, and as such is premature to summarize beyond stating that extensive testing of methods to calculate excited states and conduction/valence band edges in transition metal oxides have been carried out, along with preliminary electron/hole mobility studies. These preliminary studies are necessary to establish what theory can be trusted when performing photocatalyst modeling, which entails a complex series of events going from light absorption to produce electron-hole pairs, electron-hole pair separation and transport, followed by redox chemistry at the surface of the catalyst. Surface studies are just beginning, with characterization of structures and work functions of transition metal oxides. Adsorption and dissociation of, e.g., water, will come next.

Returning to TBCs, the key published findings during this last grant are:

- Sulfur impurities directly and seriously weaken the interface between the thermally grown oxide (TGO) and the underlying NiAl-based bond coat alloy components of the TBC due to strong repulsions between S and O electron pairs.
- Hafnium additives to the bond coat dramatically increase the adhesion of the TGO to the bond coat alloy, by forming very strong Hf-O bonds. These strong bonds are formed because of Hf's open d-shell, which allows for both polar covalent and donor-acceptor bonding to flourish. The improved adhesion is one mechanism by which Hf improves the TBC lifetime.
- Hafnium and yttrium additives readily segregate to oxide grain boundaries and block sites along the Al diffusion pathway at oxide grain boundaries, thereby slowing oxide

growth. Oxide growth continues slowly because of oxygen anion diffusion that can proceed via a different pathway. By delaying oxide growth, thermal cycling stresses due to coefficient of thermal expansion mismatches are minimized, which extends TBC lifetime.

- Hf and Y (or any early transition metal or rare earth) additives increase barriers to alumina grain boundary sliding because of their strong cross-boundary bonds to oxygen. These predictions were validated by comparison with high temperature creep measurements in polycrystalline alumina (grain boundary sliding is a key mechanism in creep). By inhibiting grain boundary sliding, these additives act to limit the tensile stress perpendicular to the TGO/bond coat interface, delaying spallation of the coating.
- Platinum additives do not directly increase TGO-bond coat adhesion nor does Pt inhibit diffusion in the oxide; Pt would rather stay in the NiAl bond coat than be found in the alumina (the TGO). This latter finding is consistent with observed growth kinetics and morphology of the TGO, both of which are unaffected by the presence of Pt. Some evidence is provided that Pt may prevent S from getting to the TGO-bond coat interface by blocking the sites S prefers.
- Pt's main role is to promote point defect (vacancies and antisite atoms) and defect cluster formation. By so doing, Pt greatly accelerates Ni and Al diffusion in NiAl, primarily by means of the triple defect mechanism, and in Ni-rich bond coats, also by the antistructure bridge mechanism. The predicted diffusivities are much larger in the presence of just a few percent Pt. By accelerating Ni and Al diffusion, Al atoms are kept in high concentration at the interface between the NiAl bond coat alloy and the TGO, even in Ni-rich NiAl alloys. By keeping the local Al concentration high, the TGO is comprised only of alumina, rather than Ni aluminate spinel. The latter is very brittle and fast growing; inhibition of its formation prevents rapid failure of the coating.

Thus, in the culminating period of the AFOSR funding for TBC research in the PI's group, a number of very important discoveries were made. The precise roles of Hf and other reactive elements, as well as that of Pt, were not known before. Although other roles for these elements may be discovered in ensuing studies, the key roles that these additives play have finally been

elucidated. Moreover, analysis of electron distributions in these materials led to basic insights into why Hf, for example, is so effective, and led to the exploration of a variety of elements not all of which are present in current bond coat alloy formulations. As a result, it was discovered that barium is extraordinarily effective at inhibiting grain boundary sliding, due to its ability to form many bonds to oxygen anions at alumina grain boundaries. Consequently, the PI has a patent pending on adding Ba to the bond coat alloy as a means to extend TBC lifetimes.

Eleven journal articles were published on this research and one spin-off patent was awarded during this grant period. One more TBC journal article is under review, a TBC patent is pending, and an invited PNAS review article is in preparation on the entire set of findings by the PI on TBCs. Twelve invited seminars on this research were given at universities, companies, and national laboratories, and ten contributed talks and posters were given by graduate students and postdoctoral fellows on this research during the grant period. The PI gave 25 invited lectures at conferences and workshops on this research during the grant period. Two graduate students who worked on TBC research, Donald F. Johnson and Kristen A. Marino, submitted their Ph.D. theses in August and September 2009, respectively. Don and Kristen are now postdoctoral fellows at Pacific Northwest National Laboratory and the University of Amsterdam, respectively. Other members of the TBC research team included Dr. Karin Carling (now an Associate Professor at Karlstad University in Sweden), Dr. Berit Hinnemann (now leader of the theory group at Haldor-Topsoe), and Dr. Ivan Milas (now a postdoctoral fellow at Dupont). The solar energy conversion group consists of Ms. Dalal Kanan, Mr. Nima Alidoust, Ms. Leah Isseroff, Ms. Peilin Liao, and Dr. Maytal Toroker (some of whom are on fellowships). Publications, patents, and presentations stemming from this work are listed at the end of this report.

Research Accomplishments

Jet turbine engine metal components are protected by a multilayer, multi-component thermal barrier coating (TBC), formed by sequential deposition of a NiAl-based bond coat alloy followed by plasma spray or electron beam deposition of yttria-stabilized zirconia (YSZ). In (Pt)NiAl bond coat based TBCs, a layer of alumina grows in between these two materials during YSZ deposition and grows further during use (this is the thermally grown oxide or TGO). Present TBCs spall off after ~16,000 hrs of thermal cycling, forcing the engine to be removed from service. If more robust TBCs can be designed, the engine could operate at higher temperature, providing either increased fuel efficiency or greater thrust. Preventing or further delaying coating failure was the main goal of this research, in order to increase the service lifetimes of aircraft engines. Our strategy has been to use periodic density functional theory (DFT) calculations to first identify inherent causes of TBC failure, then to investigate the origins of why certain additives (*e.g.*, Pt, Hf, Y) delay failure, and then to use that insight to suggest improved TBC materials that could extend coating lifetimes. DFT within the generalized gradient approximation (GGA) to electron exchange-correlation is currently the most reliable method for predicting ground state properties of most materials, as outlined in a recent *Science* Perspective written by the PI [5]; DFT-GGA is used throughout the work presented here.

Thermal cycling exposes the TBC to repeated expansion-contraction cycles, high temperature diffusion and oxide growth, which ultimately results in spallation of the coating. TBC failure is triggered by multiple events, including: (i) thickening of the alumina layer via O and Al atom diffusion from the air and bond coat alloy, respectively, subsequently producing growth and thermal stresses (caused by the thermal expansion coefficient mismatch between the metal alloy and alumina), which ultimately induce spallation at the alumina-bond coat alloy interface; (ii) impurity-induced spallation, where adhesion of the alumina scale to the bond coat is compromised by elements that segregate to the interface by high temperature diffusion. In what follows we outline the atomic scale mechanisms we have uncovered that contribute to

both failure modes and how to prevent them. We then list the personnel involved in the work (including the new solar fuels project), the articles published and presentations given during the grant period. Numbered citations refer to the publication list.

Effects of Impurities and Dopants in the NiAl Bond Coat on TGO-Bond Coat Adhesion

We evaluated with DFT-GGA the electronic and geometric structure and adhesion of the pure and doped $\alpha\text{-Al}_2\text{O}_3(0001)/\text{NiAl}(110)$ interface as a model for the TGO-bond coat alloy interface in TBCs [1]. The clean interface has a predicted ideal adhesion energy of 0.66 J/m^2 , larger by 0.2 J/m^2 than for $\alpha\text{-Al}_2\text{O}_3(0001)/\text{Ni}(111)$. The increased adhesion is due to formation of Al-O cross-interface bonds. S impurities at the interface are predicted to reduce interfacial adhesion significantly (by $\sim 80\%$!), due to a reduction in cross-interface bonds. The weakened adhesion and a spatial gap that develops at the interface helps explain transmission electron microscopy (TEM) measurements on TBCs that find S present near voids between the bond coat alloy and the oxide. The elongated, weakened bonds across the S-containing metal/oxide interface and apparent S-O repulsion induce the oxide and metal to separate and form voids upon experiencing stresses introduced during thermal cycling of the TBC. These findings provide detailed understanding of how S accelerates TBC spallation. Pt atoms at the interface, either substituting for Ni or present interstitially, weakens the interface slightly (by $\sim 20\%$), thus ruling out a previously postulated direct role for Pt of improving TGO-bond coat adhesion. On the other hand, Hf dramatically increases TGO-bond coat alloy adhesion, by forming strong Hf-O bonds across the interface, as expected from Hf's open-shell character. Our earlier work found that early transition metals such as Ti and Zr improve adhesion for the $\text{Al}_2\text{O}_3/\text{Ni}$ interface by up to a factor of two at high concentrations (0.5 ML). We found that Hf increases the metal-oxide adhesion even more, by a factor of three, even at low concentrations (0.1 ML)! Thus, one role for Hf as a bond coat additive in TBCs is a direct and dramatic increase in the intrinsic adhesive strength of the TGO-bond coat alloy interface. This also explains why Hf is a preferred dopant over Ti or Zr, since the improvement in adhesion is most pronounced with Hf.

Interaction of Impurities, Additives, and Primary Elements with an α -Alumina Surface

We used DFT-GGA to investigate adsorption of Al, O, Hf, Y, Pt, and S atoms on the $\alpha\text{-Al}_2\text{O}_3(0001)$ surface [2], as a simple model of a TGO. The electropositive metals Al, Hf, and Y all

preferentially adsorb on the same threefold hollow sites and transfer electrons to the three surface oxygen atoms. By contrast, the most stable adsorption site for the noble metal Pt and the impurity S is on top of a surface oxygen atom, with little charge transfer occurring. We find a binding energy ordering of $S < Pt < O < Al \ll Y < Hf$, which reflects the ease with which the early transition metals Hf and Y ionize and form a mixture of ionic, covalent, and donor-acceptor bonds, as well as reflecting the nearly closed-shell repulsions that weaken the adsorption of O, Pt and S. The fact that Pt binds on the same site as S, but more strongly, suggests that one role for Pt may be to displace and/or block S from segregating to the interface. Likewise, Hf and Y bind to the same site as Al, but much more strongly, suggesting that another role for Hf and Y is to block Al sites, thereby inhibiting the Al diffusion that is central to TGO thickening. Since O adsorbs on a different site, Hf and Y cannot inhibit O diffusion, which explains why these additives slow down (by inhibiting Al diffusion) but don't shut off TGO growth. Lastly, Pt does not inhibit adsorption of Al or O, which offers an explanation as to why Pt does not affect TGO growth kinetics.

Segregation of Additives and Primary Elements to an Alumina Grain Boundary

We used DFT-GGA to characterize the structure and cohesive properties of the $\Sigma 11(10\bar{1}\bar{1}) \parallel (10\bar{1}\bar{1})$ tilt grain boundary [3], which was characterized by TEM and was observed to exhibit additive segregation. This grain boundary was taken as a model for the polycrystalline alumina that grows in TBCs during operation. We then mapped out favorable adsorption sites for Al, O, Y, and Hf atoms at the grain boundary, evaluating segregation energetics and grain boundary strength as a function of segregating element. We identified a new structure for the clean boundary that is lower in energy than previously proposed structures that were based on TEM and classical potential simulations. In addition, we predicted that Y and Hf segregation to the grain boundary should hinder the diffusion of Al by blocking its preferential adsorption sites. By contrast, some adsites favored by O remain unblocked by the transition metals. Evidence for an intergranular film, reminiscent of yttrium-aluminum-garnet, was presented. Such films tend to increase stability of the ceramic. Thus, as in the simpler model above that examined Y and Hf on the alumina basal plane surface, we conclude that a major role for Y and Hf is to block diffusion of Al along grain boundaries, thereby slowing the growth of the TGO.

Effect of Pt on Defect Formation in β -NiAl

Because a direct role for Pt in increasing adhesion of the TGO-bond coat interface was ruled out above, indirect roles were examined, such as the one mentioned above in which Pt may inhibit S's ability to segregate to the TGO-bond coat alloy interface. Here we began to explore whether the main role of Pt is to affect the high temperature evolution of the NiAl bond coat alloy. It is known that Pt hinders spinel formation even in low Al content NiAl alloys. We wondered then whether Pt's role is to influence Ni and/or Al diffusion to the TGO interface in such a way as to preferentially promote formation of alumina rather than Ni spinel. We first explored Pt's effect on the formation of key defects central to postulated mechanisms of diffusion of Ni and Al through NiAl. These defects include Ni and Al vacancies and antisite atoms (Al atoms on the Ni sublattice and vice versa) and clusters of these defects [4]. Pt promotes formation of these defects, as evidenced by significant decreases in their formation energies. By decreasing defect formation energies, Pt in turn decreases the overall activation barrier to diffusion of Ni and Al in NiAl. Due to the driving force for alumina formation, Al preferentially diffuses to the bond coat alloy/oxide interface. In this indirect way, Pt keeps the local Al concentration at the NiAl surface high enough to preferentially form alumina instead of the very brittle Ni spinel, even in low Al content bond coat alloys.

Diffusion Kinetics in β -NiAl and the effect of Pt on Diffusivities

Five previously postulated diffusion mechanisms for Ni in NiAl were examined at the DFT-GGA level of theory: next-nearest-neighbor (NNN) jumps, the triple defect mechanism, and three variants of the six-jump cycle [6]. For each pathway, we calculated the activation energy and the pre-exponential factor for the diffusion constant. Although our calculations are performed at 0 K, we showed it is critical to include the effect of temperature on the pre-exponential factor. We predicted that the triple defect mechanism and the [110] six-jump cycle are likely contributors to Ni diffusion in NiAl since their activation energies and pre-exponential factors are in very good agreement with experimental data. Although the activation energy and pre-exponential factor of NNN jumps agree well with experiment, experimental evidence suggests that this is not a dominant contributor to Ni diffusion. The activation energies of the [100] bent and straight six-jump cycles are 1 eV higher than the experimental value, allowing us to exclude

both [100] cycle mechanisms. When Pt is present in the bond coat alloy [7], we find that Pt has little effect on migration energies or pre-exponential factors for any of the mechanisms listed above. However, Pt still lowers the overall activation barriers and hence greatly increases the diffusivities via reducing formation energies of defects and defect clusters that are postulated intermediates in diffusion, as already discussed above. We concluded above that the triple defect mechanism is a dominant Ni diffusion mechanism, which simultaneously results in long-range Al diffusion in the opposite direction. For completeness, however, the activation energy and diffusion constant pre-exponential factors were also calculated for all five analogous Al diffusion mechanisms in β -NiAl [11]: next-nearest-neighbor Al jumps, the triple defect mechanism and three variants of the six-jump cycle mechanism beginning with an Al vacancy. We found that the triple defect mechanism has the lowest activation energy and therefore we predicted it is the primary mechanism by which Al diffusion occurs in NiAl. The effect of Pt on each of these mechanisms was also examined. In all cases, Pt decreases the diffusion activation energy, which should enhance Al diffusion in the coatings. As argued above, this may be the main role for Pt, to enhance Al diffusion to the oxide-metal interface, keeping the local concentration of Al high and thereby forming alumina rather than brittle Ni spinels.

Effect of Dopants on Alumina Grain Boundary Sliding

We investigated the mechanism of grain boundary sliding along the α -alumina $\Sigma 11$ tilt grain boundary [8]. We identified minimum and maximum energy structures along a preferential sliding pathway for the pure grain boundary and for grain boundaries doped with a series of early transition metals, as well as with barium, gadolinium, and neodymium. We predicted that the segregation of those dopants results in a considerable increase in the grain boundary sliding barrier. Grain boundary sliding occurs by a series of bond breaking and forming across the grain boundary. Our results suggest that the presence of large cations inhibits the regeneration of bonds during sliding, which results in a decrease in total number of bonds across the grain boundary interface, thereby raising the barrier to sliding. Trends in predicted grain boundary sliding energies are in good agreement with recently measured creep activation energies in polycrystalline alumina, lending further credence to the notion that grain boundary sliding plays a dominant role in alumina creep. Moreover, we found that Ba - an element not found in

current bond coat alloys - provided the best alumina creep inhibition of all; this discovery forms the basis of a pending patent [13].

Structure and Adhesion of MoSi₂/Ni Interfaces

Our work in the early 2000s highlighted the importance of localized covalent or open-shell interactions across heterogeneous interfaces to enhance adhesion. At that time, we proposed that replacing alumina with a more covalent oxide may help TBC adhesion. Due to its propensity to limit bulk oxygen transport like alumina does (alumina's main purpose in the TBC), we considered silica as a possible replacement oxide. We found that the more covalent silica coating is much more strongly adhered to both ZrO₂ and to a Ni substrate (models of YSZ and the Ni alloys used in TBCs, respectively) than alumina is. To consider SiO₂ further, a metal silicide must be found that could provide the source of Si to be oxidized to silica. MoSi₂ has a high melting point (2030 °C) and high-temperature oxidation resistance due to a protective silica scale (which we would like to exploit). Earlier work by Jiang and Carter showed that silica is very strongly adhered to MoSi₂ (adhesion energy of ~5 J/m²) via localized covalent Si-O bonds that form across the interface, consistent with its protective properties. MoSi₂ does have a brittle-to-ductile transition in the range of 1000 °C to 1400 °C, which could be problematic, but perhaps its mechanical properties can be optimized in a thin film or composite.

We therefore evaluated the stability of molybdenum disilicide coatings on a nickel substrate, as a possible replacement bond coat alloy [9]. We considered the MoSi₂(0 0 1)/Ni(1 1 1), MoSi₂(1 0 0)/Ni(1 1 1), and MoSi₂(1 1 0)/Ni(1 1 1) interfaces and predicted quite strong (3.5–3.8 J/m²) adhesion of this metal–silicide ceramic to nickel. Mo and Si atoms at the interface are found to primarily occupy Ni 3-fold hollow sites, the typical adsorption site on Ni(1 1 1). Projected local densities of states and electron density difference plots reveal a mixture of localized, covalent Si–Ni bonds and more delocalized metallic Mo–Ni bonding, as the origin of the strong interfacial bonding. Such strong adhesion does make MoSi₂ a potential candidate for use in thermal barrier applications, in conjunction with a YSZ topcoat.

Ni and Al diffusion mechanisms in Ni-rich NiAl and the effect of Pt

We examined long-range Ni and short-range Al diffusion in Ni-rich NiAl and Pt's effect on these diffusion processes [12]. Since Ni diffusion in Ni-rich NiAl has been observed to have a lower

activation energy than Ni diffusion in stoichiometric NiAl, the antistructure bridge (ASB) mechanism is believed to be activated once a threshold concentration of Ni antisite atoms has been reached. Our calculated activation energies for Ni diffusion via the ASB mechanism agree well with experimental data, confirming that the ASB mechanism is likely operating in the Ni-rich region of the phase diagram, providing a means of long-range Ni diffusion. Since the ASB mechanism does not involve Al atoms, no long-range transport of Al occurs via this mechanism. Instead we looked at short-range Al transport via next-nearest-neighbor Al jumps into Al vacancies created during the ASB mechanism. Lastly, we predict that the presence of Pt also increases the diffusion rate via the ASB mechanism, which again suggests that Pt's role is mostly to increase transport in the bond coat alloy.

Catalyst Design Based on Metal-Ceramic Interface Characterization

Metal-ceramic interfaces are not only prevalent as protective coatings such as TBCs but are common in heterogeneous catalysis, where metal catalyst particles are bound to an oxide support. The support is typically alumina or silica, the same materials we examined for TBC applications. Ni/alumina catalysts are used for all sorts of chemical processing (methanation, hydrogenation of oils for making margarine, etc.). A classic problem is that catalysts often deactivate by sintering, where catalyst particles aggregate to form larger particles of low surface area. We had the idea that the sintering process might be inhibited if one could fasten the catalyst particles more tightly to the support. Hence adhesion characterization we did for TBCs could be applied to this completely different technology. We filed a patent on the idea that one could dope the interface between a Ni-based metal catalyst particle and a silica or alumina support with early transition metals. The idea is that the early transition metals promote stronger oxide-metal interactions via their open shell nature, which permits donor-acceptor bonding concomitant with metal-oxo and metal-metal polar covalent bonding. We had shown this to be true for alumina/nickel interfaces and postulated it to be true for other similar interfaces in the patent, which was awarded recently [10].

Diffusion of Al, O, Pt, Hf, and Y Atoms on Alumina(0001)

We investigated diffusion of Al, O, Pt, Hf, and Y on the α -Al₂O₃(0001) surface as a simple model to obtain insight into possible diffusion mechanisms occurring at alumina grain boundaries in

TBCs [14]. We calculate diffusion pathways, activation energies, and diffusion constants. For the elements involved in alumina growth, we find that Al diffusion is facile and involves a simple hop from one most stable adsorption site to the next without local minima in between whereas O diffusion has a much higher barrier and has local minima along the minimum energy pathway. This trend is consistent with relative rates of diffusion at alumina grain boundaries. Regarding common dopants in the metal (bond coat) alloy substrate from which alumina grows, we predict that Pt diffusion is facile but thermodynamically disfavored relative to Pt remaining in the bond coat alloy, while Hf and Y diffusion involve much higher barriers than Al diffusion. These results offer further explanations of experimental observations: (i) Pt's fast diffusivity and preference to remain in the metal alloy explains why Pt has no effect on alumina growth rates or morphology, which are determined by diffusion of other elements instead; (ii) Hf's and Y's slow diffusivities and similar pathways to Al diffusion shows that another role for these early transition metals is to slow alumina's growth rate by blocking Al cation diffusion that would lead to reaction with oxygen to produce more alumina.

Personnel

Faculty: Emily A. Carter, P.I.

Postdoctoral Fellows: Dr. Karin Carling, Dr. Berit Hinnemann, Dr. Ivan Milas, Dr. Maytal Toroker

Graduate Students: Kristen A. Marino, Donald F. Johnson, Dalal Kanan, Nima Alidoust, Leah Isseroff, Peilin Liao

Archival publications (published) during reporting period:

- [1] K. M. Carling and E. A. Carter, "Effects of segregating elements on the adhesive strength and structure of the α -Al₂O₃/ β -NiAl interface," *Acta Materialia*, **55**, 2791-2803 (2007).
- [2] B. Hinnemann and E. A. Carter, "Adsorption of Al, O, Hf, Y, Pt, and S atoms on α -Al₂O₃(0001)," *J. Phys. Chem. C*, **111**, 7105-7126 (2007). (Cover Article)
- [3] I. Milas, B. Hinnemann, and E. A. Carter, "Structure of and Ion Segregation to an Alumina Grain Boundary: Implications for Growth and Creep," *J. Mater. Res.*, **23**, 1494 (2008).
- [4] K. A. Marino and E. A. Carter, "The effect of platinum on defect formation energies in β -NiAl," *Acta Materialia*, **56**, 3502 (2008).
- [5] E. A. Carter, "Challenges in Modeling Materials Properties without Experimental Input," *Science*, **321**, 800 (2008).
- [6] K. A. Marino and E. A. Carter, "First-Principles Characterization of Ni Diffusion Kinetics in β -NiAl," *Phys. Rev. B*, **78**, 184105 (2008).
- [7] K. A. Marino and E. A. Carter, "The effect of platinum on diffusion kinetics in β -NiAl: implications for thermal barrier coating lifetimes," *ChemPhysChem*, **10**, 226 (2009).
- [8] I. Milas and E. A. Carter, "Effect of Dopants on Alumina Grain Boundary Sliding: Implications for Creep Inhibition," *J. Mater. Sci.*, **44**, 1741 (2009).
- [9] D. F. Johnson and E. A. Carter, "Structure and Adhesion of MoSi₂/Ni Interfaces: Evaluation of MoSi₂ as an Alternative Bond Coat Alloy," *Surface Science*, **603**, 1276 (2009).
- [10] Emily A. Carter and Emily A. Jarvis, *Supported Metal Catalyst with Improved Thermal Stability*. Patent No.: US 7,504,355 B2. Issued March 17, 2009.
- [11] K. A. Marino and E. A. Carter, "The effect of platinum on Al diffusion kinetics in β -NiAl: Implications for thermal barrier coating lifetime," *Acta Materialia*, **58**, 2726 (2010).
- [12] K. A. Marino and E. A. Carter, "Ni and Al diffusion in Ni-rich NiAl and the effect of Pt additions," *Intermetallics*, **18**, 1470 (2010).

Submitted Publications and Patents

- [13] Emily A. Carter and Ivan Milas, *Barium-Doped Bond Coats for Thermal Barrier Coatings*. Utility patent filed on August 26, 2008 (United States). Patent Application No.: 12/194,813.

[14] I. Milas, B. Hinnemann, and E. A. Carter, "Diffusion of Al, O, Pt, Hf, and Y atoms on α - $\text{Al}_2\text{O}_3(0001)$: Implications for the role of alloying elements in thermal barrier coatings," *J. Mater. Chem.*, submitted (2010).

Ph.D. Dissertations

Donald F. Johnson, Princeton University Ph.D. 2009. Dissertation Title: Materials Corrosion and Protection from First Principles.

Kristen A. Marino, Princeton University Ph.D. 2009. Dissertation Title: The Role of Platinum in Determining Thermal Barrier Coating Lifetime: A First-Principles Study.

These dissertations are available upon request from UMI Proquest Digital Dissertations <http://wwwlib.umi.com/dissertations/gateway>.

Invited Seminars

February 9, 2010 "New Ideas for Green Energy Solutions," Princeton Adult School, The Anne B. Shepherd Lecture Series, Princeton University, Princeton, NJ.

March 10, 2009 "First-Principles Materials Design for Energy Conversion and Conservation," Princeton Energy & Climate Scholars Meeting, Princeton University, Princeton, NJ.

Sept. 11, 2008 "Predictive Capabilities of Quantum Mechanics Based Modeling: What Such Approaches Can and Cannot Tell Us," UTRC Fellows Innovation Lecture Series, United Technologies Research Center, East Hartford, CT.

August 26, 2008 "Disentangling High Temperature Evolution of Thermal Barrier Coatings," Materials Council Seminar, Georgia Institute of Technology, Atlanta, GA.

July 3, 2008 "Disentangling High Temperature Evolution of Thermal Barrier Coatings," EaSTCHEM Lecture and CSEC Colloquium, University of Edinburgh, Edinburgh, Scotland, U.K.

June 25, 2008 "Disentangling High Temperature Evolution of Thermal Barrier Coatings," EaSTCHEM Lecture, University of St. Andrews, St. Andrews, Scotland, U.K.

- June 9, 2008 "Protecting Metals via Computational Design," PRISM/PCCM REU Seminar, Princeton University, Princeton, NJ.
- May 27, 2008 "Disentangling High Temperature Evolution of Thermal Barrier Coatings," Department of Chemistry Colloquium, Dartmouth College, Hanover, NH.
- March 12, 2008 "Disentangling High Temperature Evolution of Thermal Barrier Coatings," Division of Engineering and Applied Sciences, Materials Research Lecture, California Institute of Technology, Pasadena, CA.
- March 6, 2008 "Status and Challenges in Quantum Mechanics Based Simulations of Materials Behavior," Rohm and Haas Research Center, Spring House, PA.
- Feb. 15, 2008 "High Temperature Evolution of Thermal Barrier Coatings: Insights from First Principles Quantum Mechanics Calculations," Department of Mechanical and Aerospace Engineering Colloquium, Princeton University, Princeton, NJ.
- Jan. 10, 2007 "Origins of Failure in Thermal Barrier Coatings from First Principles," Colloquium, Princeton Plasma Physics Laboratory, Princeton, NJ.

Invited Lectures at Conferences

- April 30, 2010 "Assessing Transition Metal Oxides for PV and PC from First Principles," at the *Rutgers Energy Institute/Princeton University Solar Energy Seminar*, Princeton, NJ.
- December 5, 2009 "Computational Design of Materials for Energy Technologies," Keynote Speaker at the Princeton Research Symposium, Princeton, NJ.
- October 27, 2009 "Effects of Impurities and Dopants on Metal-Ceramic and Ceramic-Ceramic Interfaces in Thermal Barrier Coatings," at the Materials Science & Technology 2009 Conference and Exhibition, Pittsburgh, PA.
- October 27, 2009 "First Principles Diffusion Kinetics in Metal Alloys," at the Materials Science & Technology 2009 Conference and Exhibition, Pittsburgh, PA.

- August 17, 2009 "Photocatalyst design concepts from molecular biology and quantum mechanics," at the 238th American Chemical Society National Meeting and Exposition, Washington, DC.
- July 27, 2009 "Ab Initio Modeling of Segregation Processes at Metal/Oxide Interfaces," at the Gordon Research Conference on High Temperature Corrosion, New London, NH.
- July 17, 2009 "Ensuring Our Environmental Future," at the Big Ideas: Science, Innovation, and Discovery Conference, Seattle, WA.
- June 9, 2009 "Computational Modeling of Materials for Energy Applications," at the First Andlinger Workshop on Industry-Academic Collaboration, Princeton, NJ.
- May 25, 2009 "Status and Challenges in Modeling Molecules and Materials for Energy Conversion Technologies," at the 215th Electrochemical Society Meeting, San Francisco, CA.
- March 27, 2009 "The Road to Energy Independence via a Materials Revolution," at the Princeton Class Leadership Conference, Princeton, NJ.
- March 19, 2009 "Design of Robust Protective Coatings for Metal Components Subjected to Extreme Conditions," at the Computer Aided Molecular Design Conference, St. Johns, Antigua.
- February 21, 2009 "The Road to Energy Independence via a Materials Revolution," at the Princeton University Alumni Day, Princeton, NJ.
- December 16, 2008 "Road to Energy Independence via a Materials Revolution," at the Princeton Engineering Dean's Roundtable, Greenwich, CT.
- December 3, 2008 "First Principles Design of Metal Alloys and Oxides to Limit Chemical Degradation and Creep," at the 2008 Materials Research Society Fall Meeting, Boston, MA.

- November 13, 2008 "Wild and Justifiable New Concepts for Solar Energy Technologies," at the Princeton Engineering Dean's Roundtable, Palo Alto, CA.
- October 8, 2008 "First Principles Modeling of Diffusion Kinetics and Sliding of Alumina Grain Boundaries: Implications for Oxide Growth and Creep," at the Materials Science & Technology 2008 Conference and Exhibition, Pittsburgh, PA.
- August 19, 2008 "Understanding the Behavior of Metal Oxides," at the 236th American Chemical Society National Meeting and Exposition, Philadelphia, PA.
- August 12, 2008 "Insights from First Principles Quantum Mechanics Into High Temperature Evolution of Thermal Barrier Coatings," at the Gordon Research Conference on Solid State Studies in Ceramics, Andover, NH.
- May 19, 2008 "First Principles Predictions of Impurity and Defect Thermodynamics, Diffusion Kinetics, and Grain Boundary Sliding in Thermal Barrier Coatings," at the AFOSR Molecular Dynamics Contractor's Meeting, Vienna, VA.
- April 19, 2008 "First-Principles Materials Design for Energy Conversion and Conservation," at the China and the Environment: The Challenges Ahead, Solutions, and Future Research, Princeton University, Princeton, NJ.
- Jan. 29, 2008 "Dopant and impurity segregation and diffusion in thermal barrier coatings from first principles," at the 32nd International Conference on Advanced Ceramics and Composites, Daytona Beach, FL.
- Nov. 2, 2007 "Status and Challenges in Quantum Mechanics Based Simulations of Materials Behavior," at the NSF World Technology Evaluation Center US Baseline Workshop on Simulation Based Engineering and Science, Arlington, VA.
- Oct. 9, 2007 "Predictive modeling of materials at the nanoscale: What can we learn from quantum mechanics?" at the NSF Workshop on Predictive Modeling of Materials at the Nanoscale, Washington, DC.

August 19, 2007 "How insights into bonding of materials help explain high temperature evolution of materials," at the 234th American Chemical Society National Meeting, Boston, MA.

March 27, 2007 "Synergy in computational science and engineering," award address, Symposium for Computers in Chemical and Pharmaceutical Research in Honor of Emily A. Carter, at the 233rd American Chemical Society National Meeting, Chicago, IL.

Contributed Presentations

May 24, 2010 "Quantum Mechanics Modeling of Electronic Excitations in Metal Oxides," poster at the *AFOSR Molecular Dynamics and Theoretical Chemistry Contractor's Meeting*, Chantilly, VA. (presented by Dalal Kanan)

May 18, 2009 "The Role of Pt and S in Determining Thermal Barrier Coating Lifetime," poster at the AFOSR 2009 Molecular Dynamics Contractor's Meeting, San Diego, CA (presented by Kristen Marino).

July 20, 2008 "The Effect of Platinum on Al Diffusion Kinetics in NiAl," poster at the American Conference on Theoretical Chemistry, Northwestern University, Evanston, IL (presented by Kristen Marino).

March 17, 2008 "Quantum-Based Theories for Molecules and Materials in the Carter Group," poster at the PRISM/PCCM/MIRTHE/CNSA University-Industry Research Symposium, Princeton University, Princeton, NJ (presented by Peilin Liao).

Oct. 26, 2007 "The effect of platinum on diffusion in thermal barrier coatings," talk at the Chemical Engineering Graduate Student Symposium, 2007 at Princeton University, Princeton, NJ (presented by Kristen Marino).

- July 30, 2007 "The effect of platinum on diffusion in thermal barrier coatings," poster at the *Gordon Research Conference on High Temperature Corrosion*, New London, NH (presented by Kristen Marino).
- July 30, 2007 "Structure and ion segregation at an alumina grain boundary : Implication for growth and creep," poster at the *Gordon Research Conference on High Temperature Corrosion*, New London, NH (presented by Ivan Milas).
- March 26, 2007 "First principles predictions of structure and cohesion of alumina grain boundaries," talk in the Symposium for Capturing Complexity in Physical Sciences Simulation of Condensed Matter, at the 233rd American Chemical Society National Meeting, Chicago, Illinois (presented by Ivan Milas).
- March 25, 2007 "Insights into high temperature evolution of thermal barrier coatings from first principles," talk at the ACS Award Symposium for Computers in Chemical and Pharmaceutical Research in Honor of Emily A. Carter, at the 233rd American Chemical Society National Meeting, Chicago, Illinois (presented by Berit Hinnemann).
- Feb. 28, 2007 "The effects of platinum on thermal barrier coating failure," talk at the 2007 The Minerals, Metals & Materials Society (TMS) Annual Meeting, Orlando, Florida (presented by Kristen Marino).