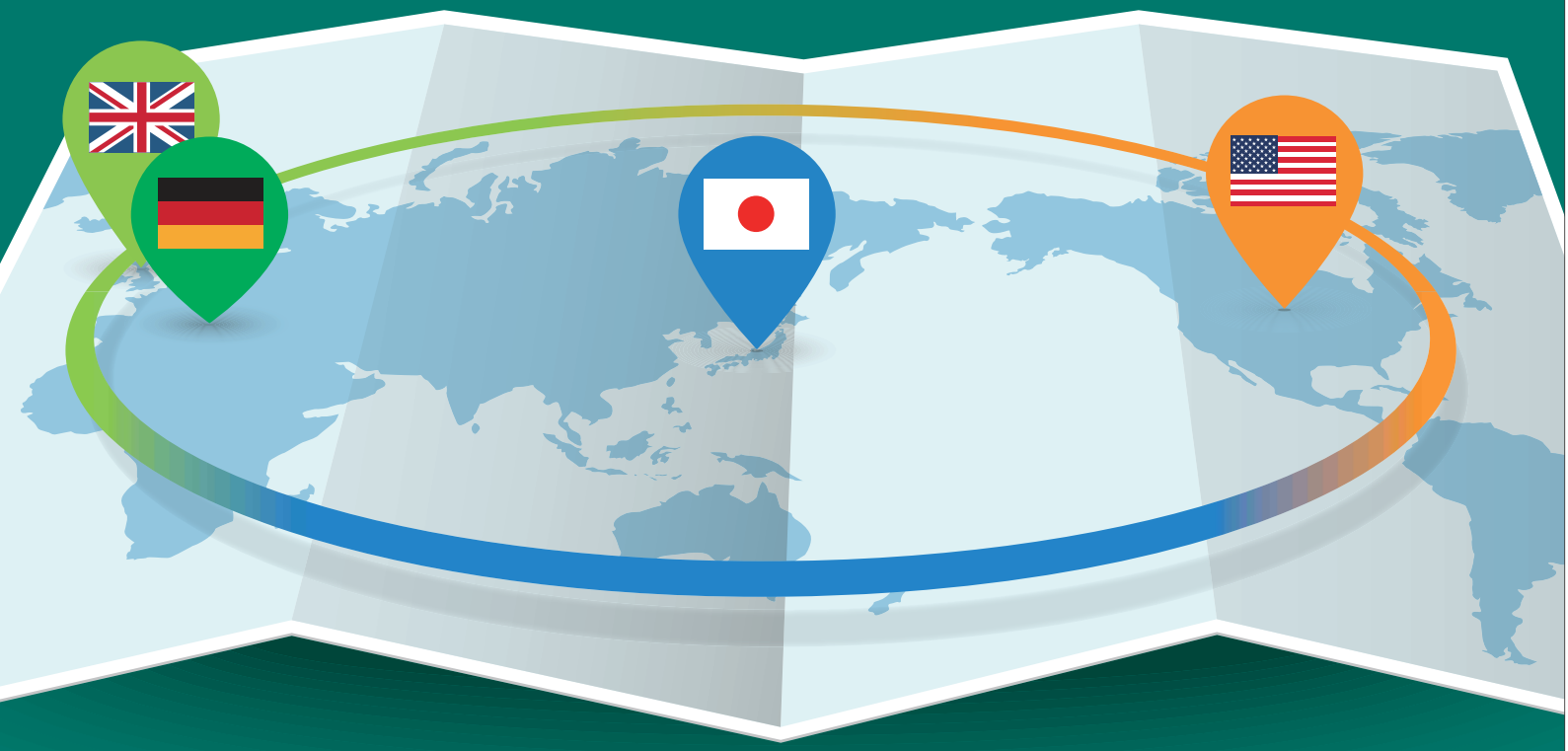
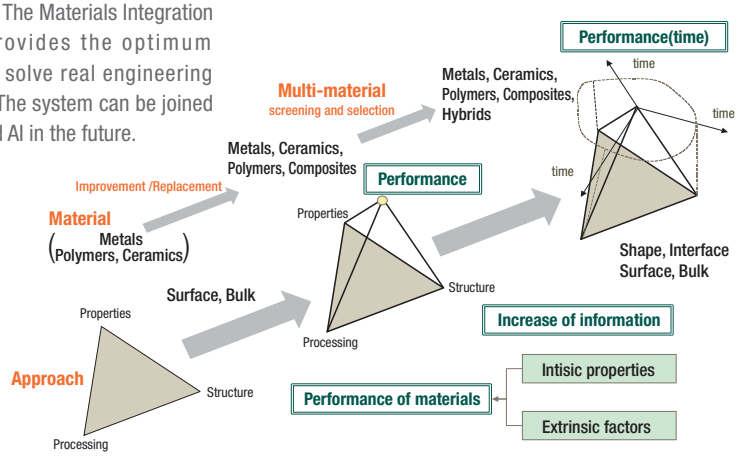
SIP-SM'4
Structural Materials for Innovation



MATERIALS INTEGRATION FOR CERAMICS COATINGS

Aiming at breakthroughs via international collaboration

The number of materials and variety of academic tools are increasing. The Materials Integration system provides the optimum solution to solve real engineering problems. The system can be joined with IoT and AI in the future.

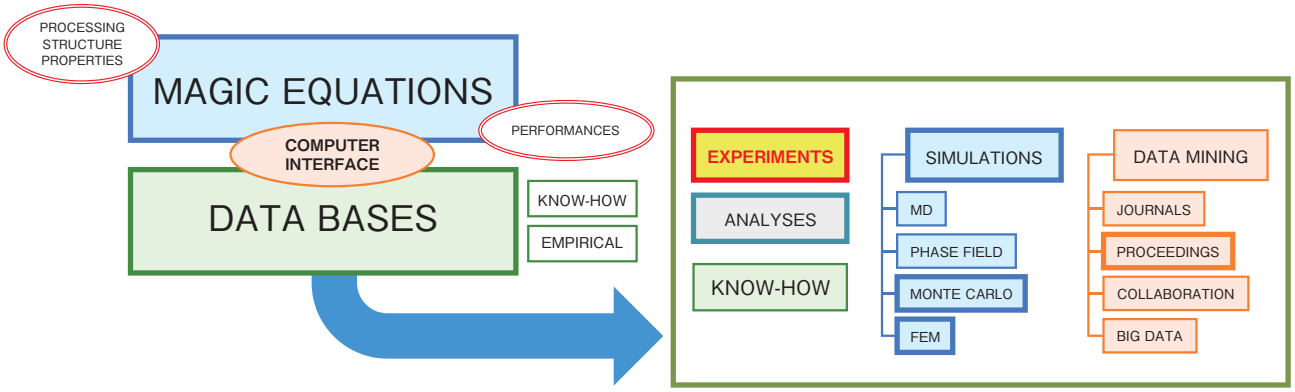


Materials Integration uses all scientific knowledge to help research and development of materials and structures. The system is designed from an engineering point of view. The system also provides information on the effect of service environment on the performance of materials and components. These computer-based estimations help to save research and development time.

Structural Materials for Innovation

SIP Cross-ministerial Strategic Innovation Promotion Program

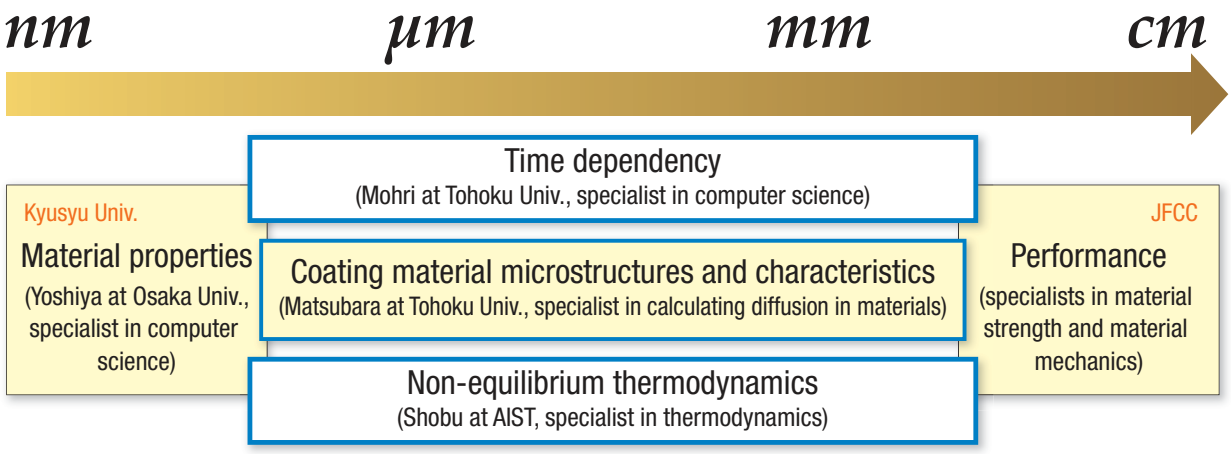
Concept & Approach



Research and Development of Materials integration (MI) covers a wide range of length scales and time scales for materials research and development of materials. Materials Integration for ceramic coatings is focused on the understanding of the link between processing, structure, properties and performance of coatings systems. The research is carried out using various kinds of available science and technology tools, such us numerical simulation, analysis, empirical forms, experiments, and know-how.

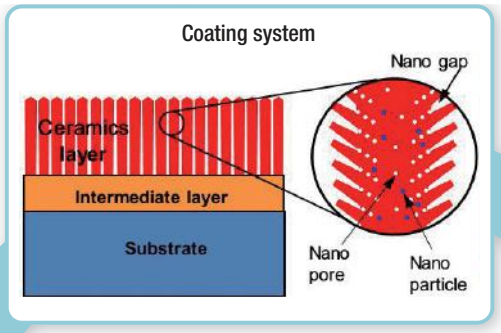
The final goal of MI for ceramic coatings is to contribute to the understanding of various behaviors of ceramics coatings and estimate the life of the coatings systems. Development of the basic system is planned in three years using thermal barrier coatings (TBCs) and then the system will be extended to environmental barrier coatings (EBCs), in which materials development is ongoing under the SIP project. Finally, MI for ceramic coating materials are expected to contribute to word-wide R&D tools for high temperature ceramic coatings.

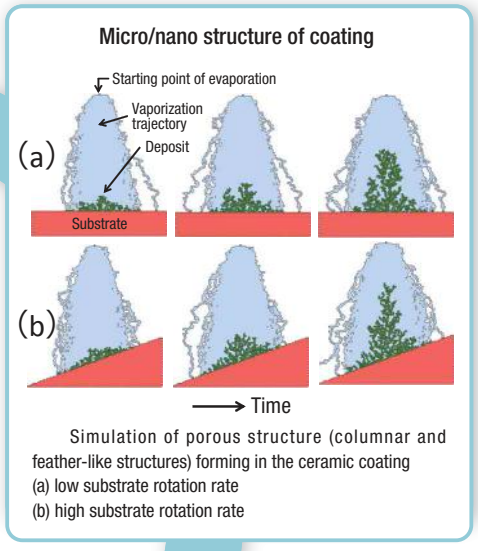
Team Members and Roles



Team members and themes for ceramic coating are reorganized the theme of performance improvement of environmental/thermal barrier coatings for aircraft engine member and its engaged researchers, in order to develop SIP innovative structural materials, as the result of establishing research themes, and selecting specialists. Thus, the new team can achieve the goals and solve problems by utilizing outcomes of research in dissimilar fields. Since the themes sufficiently address the needs of companies, and the system can support combining company-unique databases, many companies can benefit from the accomplishments.

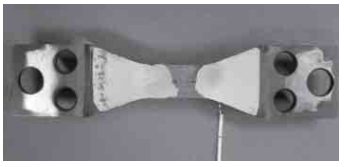
Research and Development of Ceramic Coating MI

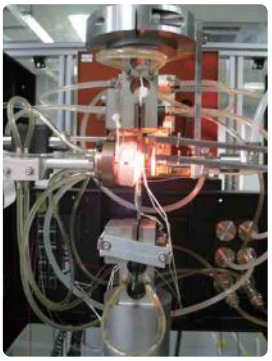




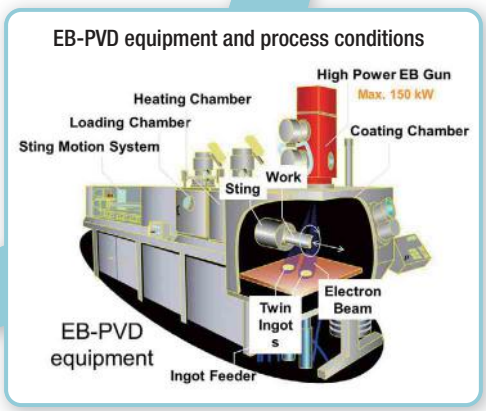
Simulation of porous structure (columnar and feather-like structures) forming in the ceramic coating
(a) low substrate rotation rate
(b) high substrate rotation rate

Spalling of coating layer
(the factor that determines the life)

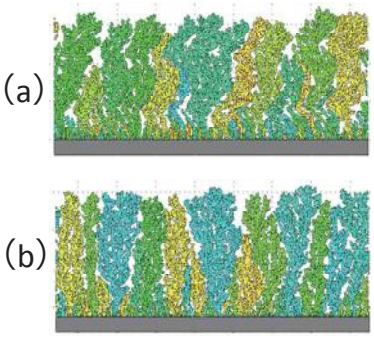




Computer simulation that predicts life based on data from accelerating tests

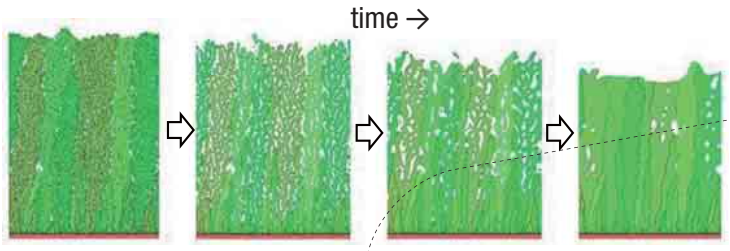


Simulation of porous structure (columnar and feather-like structures) forming in the ceramic coating

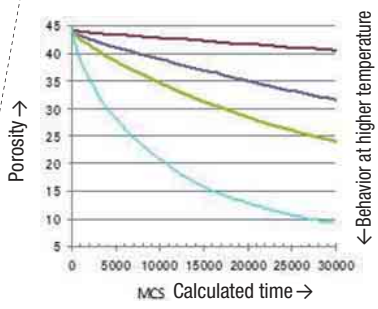


(a) low substrate rotation rate
(b) high substrate rotation rate

Simulation of sintering and microstructure change in porous ceramic layer

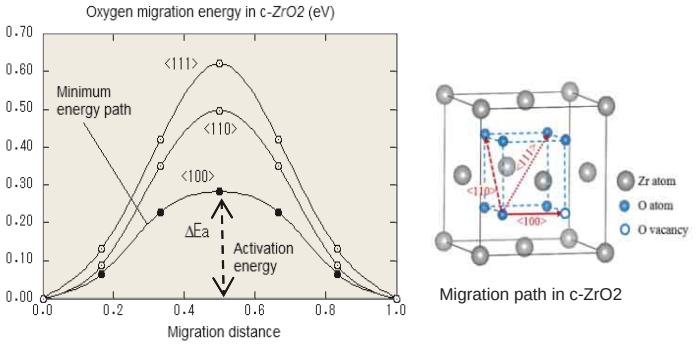


By the simulation, sintering (porosity decreasing) progress with time and temperature dependence can be quantified to predict change (degradation) in properties.



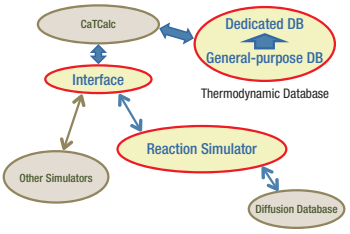
Research and Development of Ceramic Coating MI (continued)

An elementary process of time-dependent phenomenon is largely determined by a movement of a single atom. A research team (time dependency) at Tohoku University first calculates trial frequency and activation energy based on ab initio electronic structure calculation (DFT), then obtain a most probable path for a system to transit from one state to another based on the path probability method (PPM). Particularly in DFT, the nudged elastic band method and DFT are used together to obtain activation energies for several different kinds of migration paths of an atom, in order to be consistent with the path probability method based on vacancy diffusion mechanism. Furthermore, the phase field method will be applied to investigate time evolution process of the internal structure. Then, relaxation and diffusion constants will be determined based on DFT+PPM, and they will be integrated together to establish a database of thermodynamics and kinetics necessary for material designing and development.

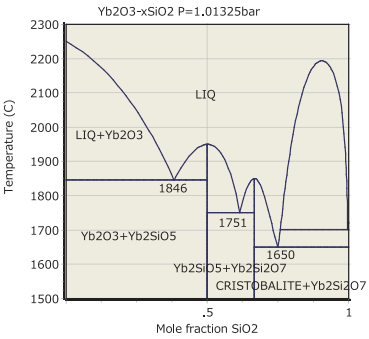


Calculation result on Activation energy of c-ZrO2
The result indicates that diffusion of oxygen atom to the (100) direction is the path with the lowest atom transfer energy.

The long-term degradation and ultimate failure of ceramic coating systems is often due to thermochemical reactions between the coating material, atmosphere, and foreign materials, and also due to interfacial reactions between layers of coating materials, which are associated with detrimental structural changes. Thermodynamic analyses are indispensable for quantitative analysis of such phenomena, and therefore, we will develop a thermodynamic database of ceramic coating systems and a reaction simulator based on the thermodynamic software, CaTCalc, which is especially suited for reaction and phase-diagram studies on ceramics. Further, we will attempt to quantify the thermo-mechanical degradation of coatings. Development of the next-generation EBC system will be substantially accelerated by such thermochemical simulation system tools to analyze coating degradation.



Database, an interface module, and a reaction simulator to be developed in the project.



Calculated phase diagram of the Yb_2O_3-SiO_2 system that contains candidate materials for EBC coating material.

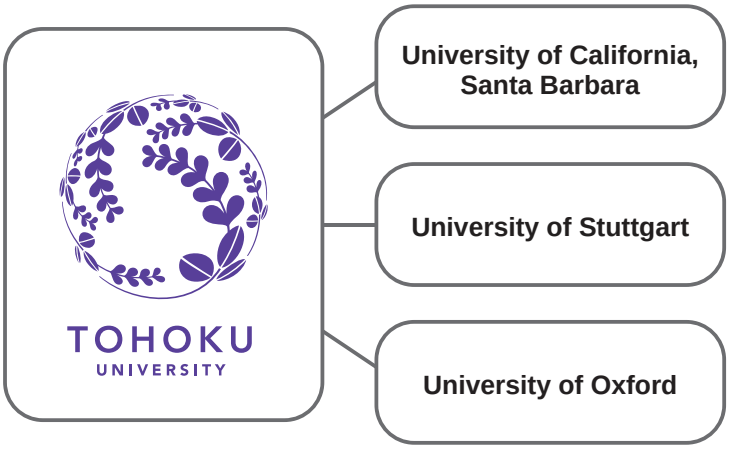
Breakthroughs with International Collaboration

The need for international collaboration

In light of its applications, such as in jet engines, ceramic coatings ideally require international collaboration from an early stage of the research for successful development and implementation.

What is expected from international collaboration.

Simulation of the techniques required to predict the life expectancy of ceramic coating as a result of damage and spalling are expected. Currently, an international collaboration involving Japan, USA, Germany and UK is being planned, with Tohoku University taking an initiative.



Japan Science and Technology Agency

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2016.02

Expectation for Materials Integration of ceramic coatings

Professor **TERUO KISHI**
Program Director

The main objective of Materials Integration (MI) for high temperature ceramic coatings is to reduce the time needed for research and development of materials-related engineering problems. The MI is expected to become a new concept tool different from traditional research and development. The MI system for high temperature ceramic coatings is a new idea and the research result is expected to contribute to cutting-edge research and development of coating technology.

Materials Integration for ceramic coatings

Professor **YUTAKA KAGAWA**
Deputy Program Director

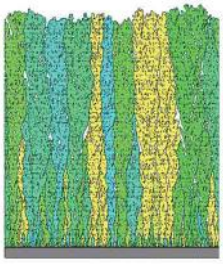
Our research on Materials Integration of high temperature ceramic coatings uses all scientific tools such as theory, experiment, analyses, simulation, database, empirical forms, etc. to solve real engineering problems. In particular special attention has been focused on the life prediction of the coating system under service conditions. The team members are experts in their respective research fields and the team has been newly organized by the SIP project. The team is expected to open new approaches of materials science and engineering of ceramic coatings in the near future.

Development of a simulation technique for investigating high-temperature mass transport and time-dependent evolution of microstructure

HIDEAKI MATSUBARA Graduate School of Environmental Studies, Tohoku University

Keyword Ceramics, Coating, Simulation, Material design, Sintering

The ceramic coating on high-temperature and high-pressure parts in aircraft engines and electrical power-generation gas turbines is investigated. A simulation technique is developed to meet industrial requests for improved properties and reliability and an optimized material fabrication process. The figure shows the simulation result of a ceramic coating whose unique microstructure is characterized by columnar and porous features. This study provides material design for microstructural changes such as pore shrinkage at high temperatures, property degradation, and peeling-off of coating layers.

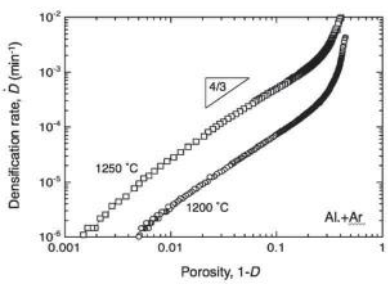


Development of a simulation technique for investigating high-temperature mass transport and time-dependent evolution of microstructure

BYUNG-NAM KIM National Institute for Materials Science

Keyword Densification、Porosity、Prediction

The time-dependent microstructural evolution of a ceramic coating is examined. The time-dependence of grain growth and porosity is observed experimentally during the densification of zirconia, and a database is developed based on the empirical equation representing the densification behavior. The figure shows the densification rate of zirconia. The slope of densification rate and the porosity is independent of the temperature. The time-dependent porosity can be predicted from the empirical relationship. The time-dependent grain size can also be predicted in a similar manner. These empirical relationships can be used as a module of the system that predicts the time-dependent microstructural evolution of a ceramic coating.

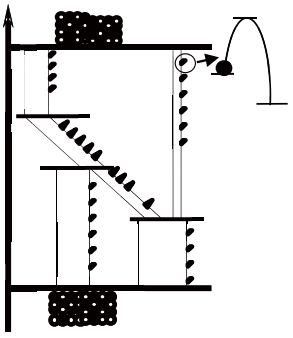


Time-dependent coarse graining and phase field parameters via path probability method

TETSUO MOHRI Institute for Materials Research, Tohoku University

Keyword: Phase field method, Path probability method, Atomic migration

The elementary process of any time-dependent phenomena may be attributed to an atomic migration event. We evaluate, via first-principles electronic structure calculations, the trial frequency and activation energy associated with the jumping of a single atomic species. The most probable time-evolution process of the microstructure is then calculated by combining the path probability and phase field methods. A kinetic database, which can be used to design and develop TBC and EBC, is subsequently developed from the calculated relaxation and diffusion coefficients. The figure shows various kinetic paths from the initial to equilibrium states; PPM determines the most probable temporal evolution path.

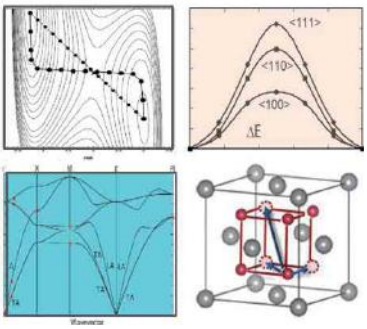


Electronic structure calculation of the elemental process of atomic diffusion

YING CHEN School of Engineering, Tohoku University

Keyword: First-principles, Electronic structure, Phonon, Activation energy, Atomic vibration frequency, Diffusion coefficient

The first-principles calculations (DFT) of atomic diffusion are performed in order to describe the time evolution process of the materials, based on the electronic structures. A series of calculations were performed for a ceramic coating material as a model system. These include: basic calculations of the phase stability and phase equilibria, evaluation of the activation energies of the elementary processes associated with atomic transfer using the Nudged Elastic Band (NEB) method, and estimation of the atom jump frequencies from the phonon vibration spectrum. The results are then combined to determine the diffusion constants (Fig.). These DFT-calculated properties will be incorporated into the DFT+PPM (path probability method) and DFT+PFM (phase field method) models, which were developed by a collaborative researcher in this project through a time coarse-graining procedure. This procedure constitutes a basic step towards establishing a theoretical tool for simulation of the dynamic processes in materials.

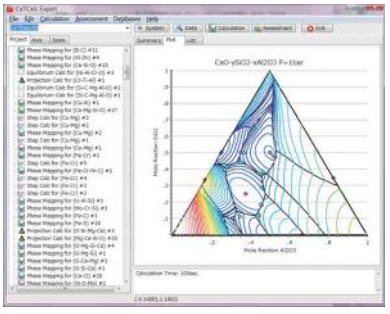


Establishment of a Domestic Technology Base for Computational Thermodynamics for Development of Advanced Structural Materials

KAZUHISA SHOBU Advanced Industrial Science and Technology

Keyword: Computational thermodynamics, Reaction simulator, CALPHAD, CaTCalc

Software modules for kinetic simulation of diffusion-controlled chemical reactions will be developed to analyze long-term thermochemical degradation of EBC. These modules are based on the thermodynamic software, CaTCalc, which is especially suited for reaction and phase-diagram studies of ceramic materials. Databases, such as the thermodynamic databases for CMAS(CaO-MgO-Al_2O_3-SiO_2)-based oxides, will also be developed for the EBC system and the physical properties. Degradation of EBC in a humid atmosphere, chemical attack by CMAS-based foreign particles, interface compatibility between the substrate and coating layers, etc., will be analyzed. Figure 1 shows the CaTCalc software.



Mechanical property evaluation of ceramic materials

HIROSHI YAMADA Advanced Industrial Science and Technology

Keyword Mechanical properties, First-principles calculation, Finite strain method

Using first-principles calculations, we investigated the relationship between the crystal structure and the mechanical properties of ceramic materials for barrier coatings (TBC, EBC). Geometry optimization was performed via the BFGS method. The string of dataset consisting of strain and stress data was then calculated by using the finite strain method. The mechanical properties, such as the elastic stiffness, bulk modulus, Young's modulus, and Poisson's ratio can be estimated by analyzing the dataset. In addition, the calculated results of some ceramic materials are listed in the table and experimental values are included for comparison. The calculated values were relatively consistent with the experimental values, indicative of the relatively high predictive accuracy.

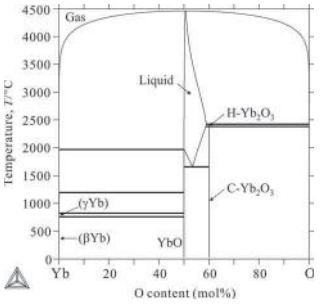
	B (GPa)	E (GPa)	ν
$SrAl_2O_4$	86 (3)	E_x=132	ν_{xy}=0.19, ν_{xz}=0.25
		E_y=121	ν_{yx}=0.17, ν_{yz}=0.35
		E_z=123	ν_{zx}=0.23, ν_{zy}=0.35
α-quartz (calc.)	42.8	E=104	ν=0.10
α-quartz (expt.)	41.1	E=102	ν=0.09
α-Al_2O_3 (calc.)	265		
α-Al_2O_3 (expt.)	267		

Development of thermodynamic database for RE-Al-Si-O system and analysis of diffusivity in ceramic coating materials

TATSUYA TOKUNAGA Kyushu Institute of Technology

Keyword Computational thermodynamics, Phase equilibria, CALPHAD, First-principles calculations, Molecular dynamics method

The aim of this work is to develop a thermodynamic database of the RE-Al-Si-O system by coupling first-principles calculations with the calculation of phase diagrams (CALPHAD) method. Furthermore, by using a molecular dynamics method, we will evaluate the diffusion coefficients of the constituent elements in ceramic coating materials that are used in airplanes. The microstructural degradation behavior of the ceramic coating during exposure to high temperatures will be predicted by the simulation, using the previously determined thermodynamic and kinetic data. An example of the obtained results, i.e. the calculated Yb-O phase diagram, is shown in the figure on the right. [Member：T. Tokunaga, S. Iikubo, M. Hasebe]

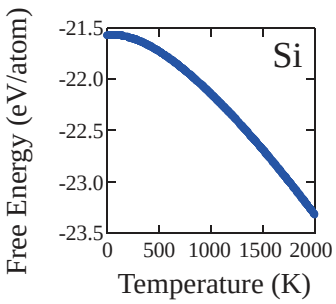


First-principles calculation of the thermo-dynamic properties of Yb_2O_3-SiO_2-based oxides

HIROSHI OHTANI Institute of Multidisciplinary Research for Advanced Materials, Tohoku University

Keyword first-principles calculations, quasi-harmonic approximation, Debye-Grüneisen approximation, Genetic algorism, free energy calculations

The free energies of oxides, at finite temperatures, are evaluated from first-principles calculations. The Debye-Grüneisen model and the quasi-harmonic approximation are applied to obtain the entropy values resulting from the lattice vibration effect. Moreover, the configurational entropy of the atomic arrangement is obtained by the cluster expansion and cluster variation methods. The free energies of each phase can be obtained by taking the entropy evaluated from these techniques into consideration. The figure shows the calculated free energy of pure Si at finite temperatures, when the contribution of the lattice vibration as calculated by the quasi-harmonic approximation is considered. The calculation procedure is used to construct a thermodynamic database of Yb-based complex oxide systems.

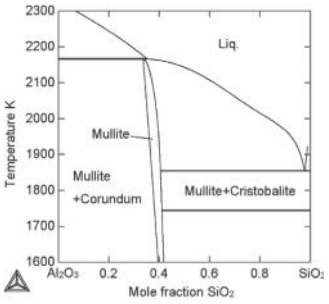


Database for the phase diagram of the Si-Al-O-N system

KATSUNARI OIKAWA Graduate School of Engineering, Tohoku University

Keyword thermodynamic, CALPHAD, ceramics

SIAlONs are widely used in engineering ceramics, owing to their high toughness, high strength, and high corrosion resistance. Phase diagrams provide the basic information needed to optimize the synthetic process and microstructure. In addition, phase diagrams, obtained via thermodynamic calculations are useful for predicting the phase stability at various temperatures and compositions. In this study, a thermodynamic database and the phase diagram of the Si_3N_4-AlN-Al_2O_3-SiO_2 system will be built based on experimental results and ab-initio calculations, using the ionic compound energy model. An example, i.e. the calculated Al_2O_3-SiO_2 phase diagram, is shown in the figure.

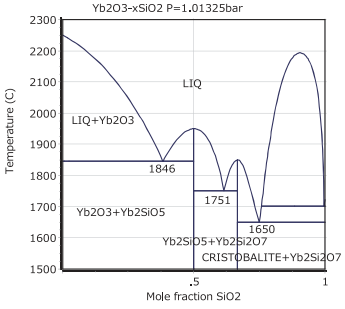


Thermodynamic assessment of Yb-based oxides based on the CALPHAD method

TAICHI ABE National Institute for Materials Science

Keyword Phase stability, Thermodynamic assessment, Yb complex oxides

A CALPHAD-type method is used to perform thermodynamic assessments of Yb-based complex oxides, which have significant potential for use as the top-coat material in environmental barrier coatings (EBC). Our target system, Yb_2O_3-SiO_2-Al_2O_3, and the three constituent pseudo-binary subsystems are critically assessed. The obtained Gibbs energy of the phases will be compiled in a database format, which can be used for various thermodynamic calculations in the CaTCalc software. The figure on the right shows the Yb_2O_3-SiO_2 pseudo-binary system that was calculated by using the Gibbs energy functions obtained from the CALPHAD-type assessment performed in this work.



Fundamental Properties of High-Temperature Ceramic Materials by Massive Computations of Materials Science

MASATO YOSHIYA Graduate School of Engineering, Osaka University

Keyword First-principles calculation,EBC,Interface crack propagation

Fundamental properties of high temperature ceramic materials are to be revealed. Thermodynamic stabilities of structures and phases, mechanical properties and thermal properties are examined by ab initio calculations. Those are used to acquire guidelines to optimize ceramic coating systems. The figure shows the charge density distribution at the cleaved surface of weakest cohesion in $RE_2Si_2O_7$ obtained by ab initio calculations where strong covalent bonding is observed. It also implies contributions of O_2 gas and moisture to crack propagation at high operating temperatures at the top and bottom of the figure. These calculations enable us to understand whether structural transformation takes place, the impact of high-temperature O_2 or moisture on the crack propagation and the ideal values of thermal stress during thermal cycling. By using this information to interpret phenomena observed by experiments, we play important roles together with experimentalists to optimize the performance of EBC and related systems.