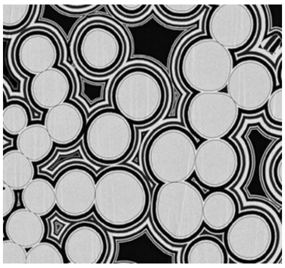
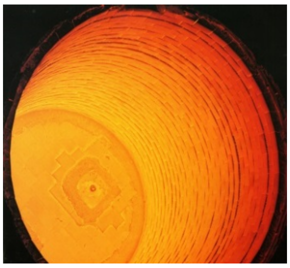
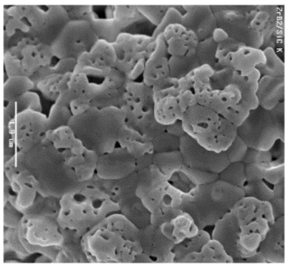





Detailed Program

ECerS Summer School

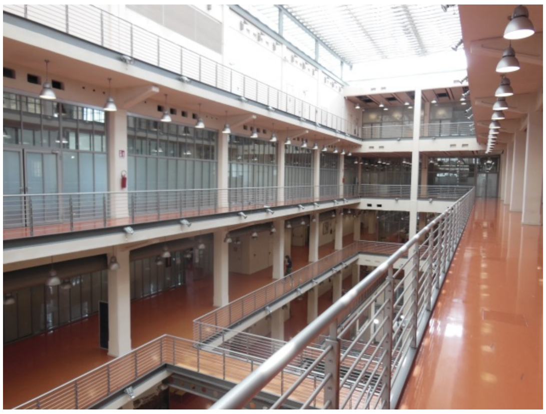
High and ultra-high temperature ceramics: reactivity and corrosion

Turin, Italy, from Friday 14th to Saturday 15th June 2019

Politecnico di Torino, Lingotto Building

Address

Politecnico di Torino, Lingotto Building
Via Nizza, 230
Torino, Italy



Lecturers

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Dr Thorsten Tonnesen	RWTH, Aachen, Germany	tonnesen@ghi.rwth-aachen.de

Program of Friday 14th June

08:00 – 08:30 Welcome and Registration

8:30-8:45: objectives and description of the training course *Pr. J. Poirier*

Design, Characteristics, applications and degradations of High and ultra-high temperature ceramics

8:45 – 9:30 Refractories *Pr. M. Rigaud*

9:30 – 10:15 Ultra-high temperature ceramics *Dr M. Balat Pichelin and Dr F. Monteverde*

10:15 – 10:30 Break

10:30 – 11:15 Ceramic matrix composites *Pr. F. Rebillat*

Thermodynamics and modelling

11:15 – 12:30 Thermodynamics of High and ultra-high temperature ceramics: phase diagrams, chemical reactions, computational thermodynamic database *Pr. I-H. Jung*

12:30 – 14:00 Lunch and Visit of the Top of the Fiat Building

Reactivity and corrosion of refractory ceramics

14:00 – 15:15 Reactivity and corrosion of refractories by gas: reactions, mechanisms, applications *Pr. J. Poirier*

15:15 – 16:30 Reactivity and corrosion of refractories by liquid (slag, metal, molten salts): reactions, mechanisms, applications *Dr T. Tonnesen*

16:30 – 16:45 Break

Reactivity and corrosion of ceramic matrix composites

16:45 – 18:00 Self-healing in ceramic matrix composites *Pr. F. Rebillat*

18:00 – 19:00 Poster session and group discussion

20:00 Banquet altogether

Program of Saturday 15th June

Reactivity and corrosion of ceramic matrix composites

8:30 - 9:45 Recent progress of environmental barrier coatings: achievements, open problems and challenges *Pr. Y. Kagawa*

9:45 -11:00 Processing of carbon-fibre based UHTCs and thermo-ablative materials testing by oxyacetylene and oxypropane testing, arc jet testing *Pr. J. Binner*

11:00 -11:15 Break

Reactivity and corrosion of ultra-high ceramics

11:15-12:30 Study of the high temperature behaviour of ultra-high temperature ceramics and the measurements of emissivity and catalycity (atmospheric reentry of space vehicles)
Dr M. Balat-Pichelin

12:30 – 14:00 Lunch

14:00 –15:15 Thermo-chemical surface (in)-stabilities of ultra-high temperature ceramics in simulated reentry conditions *Dr F. Monteverde*

15:15 – 15h30 Break

15:30 –16:45 Entropy stabilized ultra-high temperature ceramics: oxidation and transport properties *Pr. E. Opila*

16:45 – 18:00 Group discussion, conclusion, Contest winners and closing

Content

1. Design, Characteristics, applications and degradations of High and ultra-high temperature ceramics

1.1. Refractories by Pr M. Rigaud

This presentation is divided into 3 parts starting with 1) Reactivity 2) Design of refractories 3) Corrosive degradation.

Part 1- Reactivity # Stability= Thermodynamic-Equilibrium # Non-Equilibrium =Kinetics.

- The fundamentals. At 450 C < T < 1700 C
- Thermodynamics, the chemical potentials: phases and interfaces, wetting and surface Chemistry, Kinetics
- The global constraints : thermal- chemical- mechanical Gradients. The coupling of the three
- The Applications. Refractories as Heat Container and Safety Engineered Materials

Part 2-Design and Characteristics.

- What are Refractories: coarse grain aggregates (2/3) fine grain matrix (1/3) plus pores (at temperature of use: 8 to 20% for dense, 25 up to 50 % for insulating). A lot of interfaces!
- The recipes. Select aggregates: purity, crystallinity, high melting and sinter- Ability
- Select matrix materials: the binders and adjuvants.
- Select the manufacturing procedures: fired- and non-fired; shaped- and non-shaped.
- Differentiate between lining and refractory specimen and the modes of degradation.
- The Characteristics and Properties
- Properties-Temperature-Time-Sensitive
- The Characteristics and the role of the installation methods and the variability of the operating parameters
- Different gases

Part 3- The Corrosive Degradation of refractories under continuous corrosion.

- Dissolution under chemical potential gradients and penetration under pressure and surface energy gradients
- Evaluation Methods: macro- meso and micro levels.
- The Impacts of Corrosion Damages
- The Concluding remarks and Prospective New Researches.

1.2. Ultra-high temperature ceramics by Dr M. Balat Pichelin and Dr Frederic Monteverde

Ultra-high temperature ceramics

- Definition
- Elaboration processes
- Properties (mechanical, thermal and optical)
- Main uses

Focus of F. Monteverde on the elaboration techniques used at ISTEC (30 min)

1.3. Ceramic matrix composites by *Pr. F. Rebillat*

Ceramic matrix composites (CMC) refractory composite materials are combining refractory fibers embedded in a refractory matrix made of a single or few ceramics to meet extreme conditions.

The introduction of a fibrous reinforcement allows to toughen the matrix material. Thus, mechanical properties are attractive even at high temperatures and for densities four times lower than super alloys. They are also very resistant to oxidations and irradiations. Extreme conditions in aerospace, space or nuclear fields are their main application domains. Depending on the application, the temperature of use is between 400°C to more than 2000°C in oxidative atmosphere (air, jet engine combustion gas...). The material can be subjected to stresses of more than 200MPa. This stress can also be complex (fatigue loading, vibrations, multiaxial stresses, high temperature gradients...). Operating times can be from a few minutes for solid propulsion to tens of thousands of hours for civil applications (aeronautic, nuclear...). The final properties and the respective domain of applications of these composites are highly related to the compositions, the architecture and the processes of the different constituents

Fibers that are essentially carbon (C), silicon carbide (SiC) or oxide (alumina, basalt, mullite) fibers hold most of the load applied. Thus, failure properties of those composite highly depend on the thermo-mechanical and thermal-stability of fibers. The properties of fibers are controlled through its composition, its purity and its degree of crystallization.

The historic process to impregnate preform by a matrix is chemical vapor infiltration (CVI). This process is used in particular for carbon, silicon carbide and multilayered matrixes. The advantage of CVI is to obtain a very stable and dense matrix, but the process is very long, expensive and a residual porosity remains. Liquid impregnation processes were also developed either from infiltration and sintering of powders, from melt or reactive melt infiltration (MI or RMI) of liquid Si or from pyrolysed polymeric precursors. After the pyrolysis of the precursor, the porosity left is important and the mechanical and protective properties are weak, yet fibers play a clear reinforcement role.

A third component must generally be added not to obtain a material as brittle as a monolithic ceramic. It is the job of the interphase. This thin phase placed between the fiber and the matrix is easily cleavable. The interphase must be strong enough to transfer the load to fibers and weak enough to prevent crack propagation in the armour and fiber breakings. The interphase must also protect fibers against oxidation. This interphase gives the composite its tenacity and its behaviour is damageable, which prevents the brutal failure of fragile materials.

2. Thermodynamics and modelling

by Pr In-Ho Jung

Thermodynamics of High and ultra-high temperature ceramics: phase diagrams, chemical reactions

- Understanding of Phase diagrams
- Chemical reactions between solid, liquid and gas
- Computational Thermodynamic Database

3. Reactivity and corrosion of refractory ceramics

3.1. Reactivity and corrosion of refractories by gas: reactions, mechanisms, testing, applications by Pr. J. Poirier

The corrosion of refractories by gas concerns several industrial applications. These include iron works, glass making, non-ferrous metallurgy, cement production, energy production (combustion, gasification) and waste processing. Corrosion by gas can be very severe, sometimes even more so than corrosion by liquids or solids. The properties to be considered with respect to gas corrosion are porosity, pore size and permeability of the refractories. What is important is the total surface area exposed to the corrosive gases. If the corrosive gas can penetrate the refractory easily, the exposed surface area is increased significantly, and corrosion is thus accelerated.

This presentation is divided into 3 parts:
1) Fundamental mechanisms of corrosion,
2) Reaction inventory and key factors of corrosion
3) How to limit the gaseous corrosion?

Part 1 - Fundamental mechanisms of corrosion
Gas corrosion of the refractory involves four basic reactions that occur one after another:

- Physisorption
- Chemisorption
- Diffusion through the product layer formed
- The reactions at the internal interface

Part 2- Reaction inventory and key factors of corrosion
Refractory corrosion by hot gas, vapors and dust involves multiple reactions. The type of corrosive atmosphere may vary with the different vessels and with local conditions:

- Oxidizing or reducing environment
- Alkali containing environment
- Halogen or/and chalcogen environment
- Vacuum
- H_2O vapor
- Various metallic vapors: H2O, Zn, Pb, Si, Mg, etc...

Part 3 - How to limit the corrosion?
By studying chemical reactions and mechanisms, we can learn better how to control corrosion that provides a maximum refractory service life with a minimum cost. Fundamentally, kinetics predominates, even if thermodynamics is to be considered. Thermodynamic calculations are a valuable indication of whether a refractory is stable or not in an environment.

Obviously, knowledge of kinetics is useful when deciding whether a refractory will be chosen for a specific industrial application. However, caution should be taken when interpreting the results if the laboratory experimental conditions differ in any way from those in the proposed application, and it is very desirable that any kinetic experiments carried out should simulate the conditions of use as closely as possible.

3.2. Liquid-solid interactions of refractories with steel and slag - microstructural influence, direct and indirect dissolution, decarburization, testing by Dr T. Tonnesen

The liquid-solid interactions of refractories are explained in the range from fundamental descriptions until microstructural expressions in case studies and industrial trials. Following parts are discussed in particularly.

Microstructural Influence:
- Interfacial Energies
- Coating
- Wetting
- Infiltration
- Disintegration
- Anisotropic Wetting
- Influencing Parameters and Temperature Dependence

Dissolution/Solubility:
- New Phase Formation
- Saturation
- Direct/indirect dissolution
- Reaction Control
- Examples: Alumina, Spinel, MgO

Chemical stability:
- Interpretation of Fundamental Data: Phase Diagrams and Richardson-Ellingham Diagrams
- MgO-C-Materials
- Phase equilibrium: MgO-C +Al
- Contact to steel

Slag corrosion :
- MgO microstructure
- Slag Basicity
- Oswald Ripening
- Decarburization and Oxidation
- Validation by Testing Methods

4. Reactivity and corrosion of ceramic matrix composites

4.1. Self-healing in ceramic matrix composites by Pr F. Rebillat

Ceramic Matrix Composites such as SiC/SiC are proposed for applications in the aeronautical and space domains because of their thermomechanical properties and their resistance to corrosive atmosphere. More recently, a multilayer Si-B-C ceramic matrix, constituted by a succession of B4C and SiC layers, has been developed to provide self-healing properties to the new composite onto a wide range of temperature. The matrix cracks represent pathway for oxygen diffusion up to fibers. The incorporation of boron bearing species such as B4C in the matrix allows a self-healing process of these cracks from temperatures around 500°C by formation of B2O3, a liquid oxide. However, in presence of water vapour, boron oxide forms gaseous hydroxide species leading to a reduction of the self-healing capability.

Our objective is to give a scientific approach to define the environmental conditions to get a seal-healing, applied to these latter composites. Under moist air, the sealing appears as a compromise between a quick poorly stable boron-enriched oxide formation and a slower generation rate of a much more chemically stable boria-containing phase.

Firstly, the methods to extract a kinetic law from weight measurements are given at high temperature in a dry or wet environment. Then, it is necessary to progressively study: (i) the oxidation behaviour of the different components and (ii) the oxidation behaviour of this multi-layered matrix, in dry and wet atmospheres. Moreover, in order to study the role of each boron carbide-containing constituent in the self-healing mechanism of a composite, it is proposed to work with a planar crack in the SiBC ceramic matrix composite. The evolution of efficiency of the self healing is illustrated through the change of: composition of gaseous environment, gas velocity and size of a matrix crack.

4.2. Recent progress of environmental barrier coatings: achievements, open problems and challenges by Pr. Yutaka Kagawa

Recently, environmental barrier coatings (EBCs) have been applied for advanced aero-engine CMC components, and EBCs are expected to protect CMC components from harsh environments. Understanding of the achievements on the past researches band current researches, especially solved and unsolved problems, are very important. The lecture is focused on the past achievement of research results of the performances of EBCs, history of EBC technologies, some recent topics related to new materials and processing of EBC, and future direction of advanced new type of EBC. Under service, both physical and chemical damages are introduced into EBC and CMC substrates, degradation mechanism of EBC, including substrate CMC is also discussed in terms of intrinsic and extrinsic damages. Delamination problem from CMC substrate is also included in the lecture, especially life prediction point of view.

4.3. Processing of carbon-fibre based UHTCs and thermos-ablative materials testing by oxyacetylene and oxypropane testing, arc jet testing by Pr J. Binner

There is an increasing demand for advanced materials with temperature capability over 2000°C in highly corrosive environments for aerospace applications. As one example, rocket nozzles of solid or hybrid rocket motors must survive critical thermal, chemical and mechanical environments produced by high performance solid propellants. Some propellants are highly corrosive and typical flame temperatures range from 2700 to 3500°C. The interaction of environmental conditions together with the requirement that dimensional stability of the nozzle throat is maintained makes the selection of suitable materials extremely challenging. Similarly, thermal protection systems (TPS) for space vehicles flying at hypersonic (i.e. greater than Mach 5) speeds must be able to withstand temperatures up to 2300°C, intense heat fluxes (1-15 MWm^{-2}) and mechanical stresses associated with vibrations at launch and re-entry into Earth's atmosphere. The combination of extreme temperature, chemically aggressive environments and rapid heating / cooling is beyond the capabilities of current engineering materials. What is needed is the design, development, manufacturing and testing of a new class of Ultra High Temperature Ceramic Matrix Composites (UHTCMCs) based on C fibre preforms combined with ultra-refractory ceramics (UHTC) suitable for application in severe aerospace environments.

Recent work has focused on the fabrication of UHTCMC composites using a range of different techniques. These have included impregnating carbon fibre preforms with UHTC powders and then sintering them; impregnating the preforms and then filling the void space with a carbon or UHTC matrix via chemical vapour infiltration (CVI); filling the void space using reactive metal infiltration (RMI), and filling the void space using polymers that are subsequently pyrolysed to yield ceramics (PIP). All four of these routes will be reviewed, with their advantages and disadvantages outlined.

Once made, these materials need testing and a number of different approaches are used – for example, simply heating the materials in air in a furnace, however this bears little relation to the actual end-use of the materials. By far the best approach is the arc-jet, which subjects the materials to conditions very similar to what they will see in their end-application. However, testing can be extremely expensive and results can take several weeks to appear. What is needed is a rapid, low cost test system that can be used to screen materials; eliminating those that do not perform well and allowing those that pass the tests to be subjected to the arc-jet with confidence since it is known that it is worth the time and cost. Oxyacetylene and oxypropane torches have been developed specifically to provide such testing regimes and these will be outlined, together with their advantages and disadvantages.

5. Reactivity and corrosion of ultra-high ceramics

5.1. Study of the high temperature behaviour of ultra-high temperature ceramics and the measurements of emissivity and catalycity (atmospheric reentry of space vehicles) by Dr. M. Balat Pichelin

Some UHTCs are developed to be used for space application when high temperatures and extreme aggressive environments are present. This lecture will present the behaviour of some UHTCs in air plasma conditions partially simulating the atmospheric re-entry of space vehicles. During the atmospheric re-entry, the recombination of atomic oxygen present in the air plasma will lead to possible recombination to form the oxygen molecule and this phenomenon take place on the materials surface. This recombination being highly energetic, one part of the reaction heat can be transferred to the material and thus this catalycity must be evaluated

(recombination coefficient and heat flux) to be implemented in the design and trajectory calculation of the vehicle. Another important parameter to know is the emissivity at high temperature (up to 2500 K), this parameter being involved in the heat transfer.
The different reactors (MESOX and MEDIASE) developed for these measurements will be described together with the presentation of some results obtained on several UHTCs.

5.2. Thermo-chemical surface (in)-stabilities of ultra-high temperature ceramics in simulated reentry conditions by Dr. Fr. Monteverde

- Thermo-chemical stability tests in equilibrium conditions: set-up, results and interactive discussion
- The re-entry: brief introduction, and description of an arc-jet testing gallery
- Thermo-chemical stability vs instability of UHTCs in simulated reentry conditions: set-up, diagnostics, results and interactive discussion.

5.3. Entropy stabilized ultra-high temperature ceramics: oxidation and transport properties by Pr. Elizabeth Opila

Ultra-High Temperature Ceramics (UHTCs) are proposed for use in challenging environments, such as hypersonic vehicles, where operating temperatures can exceed 2000°C.

To meet the high temperature needs of hypersonic applications, UHTCs are typically composed of group IV, V, and VI transition metal carbides, nitrides, and borides. Considerable progress has been made over the last decades to improve the synthesis and mechanical properties of these materials; however, their poor oxidation resistance remains a barrier to use in hypersonic applications.

Multi-component UHTCs have recently become a topic of research interest, broadening the composition space for potentially improved material properties.

This presentation will first describe the concept of entropy stabilization and the potential for improved material properties of entropy stabilized materials. Important considerations for oxidation of ES-UHTCs (Entropy Stabilized UHTCs) and experimental results for five-component carbides and borides will be discussed next. Particular points of focus include the relative thermodynamic stability of the oxidation products of these multicomponent ES-UHTCs and how thermodynamic considerations are reflected in both the oxidation products and the depletion of the underlying material. Finally, the kinetics of the oxidation reaction for ES-UHTCs will be addressed, exploring both transport in the oxide scale and the underlying substrate materials.