Publishable Summary for 17IND11 Hi-TRACE
Industrial process optimisation through improved metrology of thermophysical properties

Overview

Many industries such as space, aeronautics, nuclear energy and glass operate installations at temperatures above 1500 °C. In order to optimise their processes and increase their competitiveness, these industries are developing new materials able to work at higher temperatures. The overall objective of the project is to establish a metrological infrastructure composed of reference facilities in order to provide industries with traceable thermophysical properties data of any solid material up to 3000 °C. The project outputs will enable European industries to significantly increase energy efficiency, reduce gas emissions, enhance safety and improve reliability of critical applications.

Need

Over recent years, the operational temperatures of process plants or components in safety-critical applications have been increased to higher temperatures, e.g. above 1500 °C.

- In space applications, space modules need reliable thermophysical properties data (thermal diffusivity, specific heat, emissivity and temperature of fusion) at temperatures as high as 2500 °C, for optimising re-entry vehicle designs. ArianeGroup has shown that numerical models may overestimate the temperature of the shield of re-entry vehicles by 600 °C. Adapted models and accurate thermophysical properties data are necessary to achieve a better prediction.
- In nuclear applications, the use of current Zirconium-based alloys is very common for manufacturing fuel cladding. Silicon carbide based composite materials are seen today as one promising alternative for the use of Accident Tolerant Fuel as their oxidation temperature is far higher than that of Zirconium-based alloys (approximately 2000 °C vs 1200 °C). Knowing the thermal diffusivity and specific heat of these 3D non-homogeneous composite materials is crucial for predicting their behaviour in industrial conditions.
- In gas turbines many design factors influence the overall efficiency but a major step has been achieved by increasing the engine temperature by 7 % when using thermal barrier coatings. However, for these coatings the state of bonding (which influences the thermal resistance between interfaces) is very critical for their operability, as the materials are used close to their temperature limit. A discrepancy of a few degrees significantly changes the operability of a gas turbine.

In the examples mentioned above, no traceable thermophysical properties measurements exist at very high temperatures (above 1500 °C) for assessing uncertainties of the measured values. In order to fill this gap, it is necessary to develop metrological tools based on reference facilities with their corresponding uncertainty budgets, and to validate new measurement techniques using reference materials and comparisons with reference facilities.

Objectives

The aim of the project is to increase the traceability to the SI of thermophysical properties measurements at very high temperature through reference facilities, new set-ups, calibration methods, uncertainty budgets and reference materials.

The specific objectives of Hi-TRACE project are:

1. To establish a reference facility based on laser flash method for the traceable measurement of thermal diffusivity of solid materials between 1500 °C and 3000 °C, and to determine an uncertainty budget.

2. To develop validated methods and establish reference facilities (based on drop calorimetry or laser flash method) for the traceable measurement of specific heat of solid materials between 1500 °C and 3000 °C. The target uncertainty is 0.5 % below 1000 °C and 1.5 % above.
3. To establish a reference facility for the traceable measurement of emissivity of solid materials above 1500 °C based on radiometric or calorimetric methods. The target uncertainty is 0.5 % below 1000 °C and 1.5 % above. In addition, to develop validated methods for the measurement of the melting temperature of materials up to 3000 °C.
4. To develop validated methods to quantify the mechanical adhesion of solid materials, in particular functional layers, for thermal or corrosion protection above 1000 °C via the thermal contact resistance.
5. To facilitate the take up of the technology and measurement infrastructure developed in the project by standards developing organisations and end-users.

Progress beyond the state of the art

Several National Metrology and Designated Institutes operate facilities for measuring thermophysical properties of solid materials (alloys, polymers, complex coatings etc.) in order to provide industries with certified values with associated uncertainties. *Specific heat*, *thermal conductivity* and *spectral emissivity* are measured up to 1000 °C, and sometimes up to 1500 °C. Some reference facilities have been developed and characterised in terms of metrology up to 2000 °C (in the case of thermal diffusivity) during a previous project. At the same time, device manufacturers and academic laboratories have developed and extended new measurement methods up to 3000 °C. This project will further develop reference facilities for each of these properties in order to obtain reference values for solid materials from 1500 °C to 3000 °C and to provide traceability for industrial and academic users to validate other new methods.

Temperature of fusion of most materials is known up to several thousand degrees Celsius. These values were obtained either by academic facilities or by industries themselves. However, so far, neither reference material nor reference facility exists at temperatures above 1500 °C, meaning that these measurements have been made without traceability. The project will propose methodologies with uncertainty budgets for measuring temperature of fusion of refractory materials up to 3000 °C.

De-bonding phenomena of thermal barriers applied onto turbine blades have been studied before. The existing approaches for non-contact and non-destructive techniques for quantifying the state of adhesion by using optical or infrared radiation are not satisfactory and not validated. The project will go beyond the state-of-art by providing validated measurement facilities of *thermal contact resistance*, dedicated reference artefacts and numerical tools that will be used for characterising the state of de-bonding at temperatures from room temperature to above 1000 °C.

Results

Establishment of traceability for thermal diffusivity measurements at temperatures up to 3000 °C

Two existing laser flash devices have been modified to operate at very high temperature by improving the inductive furnaces used (modification of the high frequency generator) and by implementing new bi-chromatic radiation thermometers that have been calibrated up to 3000 °C.

The performances of one of these facilities have been tested by performing thermal diffusivity measurements on graphite specimens. In a first step, comparative thermal diffusivity measurements were performed with the same specimen heated by the modified inductive furnace then by a resistive furnace, which is used in the reference configuration for measurements performed in the medium temperature range because it has better temperature homogeneity than the inductive furnace. The obtained results are in good agreement (deviation less than 1 %) in the common working temperature range (from 500 °C to 800 °C) of these two furnaces. In a second step, the thermal diffusivity of this material has been measured in the inductive furnace up to 2995 °C.

An in-situ calibration method of the radiation thermometers has been developed by using metal-carbon eutectic high temperature fixed points (HTFPs) positioned in the furnace at the location of the specimen. Different geometries of palladium-carbon (1492 °C), platinum-carbon (1738 °C) and iridium-carbon (2290 °C) fixed-point cells have been designed and used to test the proposed calibration method. Cells having the same shape and size as samples give the best results in terms of uncertainty.

Establishment of traceability for specific heat measurements at temperatures up to 3000 °C

Two drop calorimeters based on different technical solutions are under development.

In the first case, a heat flux calorimeter composed of two thermopiles was integrated in an isothermal bloc that has been positioned under an inductive furnace. A shutter system has been implemented between the furnace and the calorimeter in order to limit the radiation coming from the furnace into the thermopiles. The specimen position in the furnace has been optimized in order to improve the temperature homogeneity in the heating zone. The stability of the baseline (signal delivered by the thermopiles before the specimen drop) has been enhanced by modifying the cooling circuit of the furnace.

The heat flux calibration of this calorimeter is performed by electrical substitution thanks to crucibles equipped with a specific heater mounted as a 4-wires resistance and put in the thermopiles. A calibration of the thermopiles is carried out after each specimen drop by dissipating approximately the same amount of energy by joule effect as that released by the specimen in the calorimeter after its drop. First determinations of the sensitivity of the thermopiles by electrical calibration showed good linearity versus dissipated electrical energy. The procedure for the in-situ temperature calibration of the radiation thermometers used to measure the temperature of the specimen before its drop is the same as the one described for thermal diffusivity measurements. First specific heat measurements have been performed up to 2000 °C with this drop calorimeter on a tungsten specimen.

In the second case, the different elements of the calorimeter prototype (copper block equipped with thermistors, shutter system, induction furnace, pyrometer etc.) have been assembled. The dropping mechanism and its control (electronics, software) are under construction. Furthermore numerical simulations have been performed to evaluate the specimen's emitted heat during the free fall after the heating period in the induction furnace.

A theoretical concept for dynamic specific heat measurement based on laser flash technique was developed for samples with known spectral emissivity. It has been tested experimentally using a graphite coating deposited on tungsten samples, and a preliminary uncertainty budget was established.

A sub-second pulse-heating facility has been modified for measuring the specific heat at temperature above 1500 °C. First high temperature pulse heating measurements have been performed on pure tungsten samples up to 2300 °C using this facility. These preliminary results show good agreement with specific heat data coming from literature.

Establishment of traceability for emissivity measurements and improved metrology for temperature of fusion at temperatures up to 3000 °C

A metrological reference facility based on a calorimetric method, developed in a previous project, is under modification in order to enable traceable measurements of normal spectral emissivity at very high temperature. Materials suitable for the sample holder have been investigated and considered candidates were boron nitride**,** graphite and tungsten. As a boron nitride sample holder would be difficult to install with the current design of the setup, only graphite and tungsten sample holders have been designed. FEM (*finite element method*) simulations of the heating process towards higher temperatures have been performed. Currently the maximum tested operation temperature is 1700 °C.

Upgrades of three other existing setups based on radiometric approach are in progress and these systems for emissivity measurements will be compared to the reference one through the inter-laboratory comparison.

Solid homogeneous materials have been selected by the consortium to be used for the three inter-laboratory comparisons on thermal diffusivity, specific heat and emissivity measurements that will be organised in the second part of this project. The selected materials (molybdenum, tungsten and isotropic graphite IG210), which were chosen due to their high melting points, could be candidate reference materials for calibration at very high temperature of laser flash apparatuses, calorimeters and emissivity measurement devices. The specimens needed for the three inter-laboratory comparisons (about 75 specimens per material) have been machined in the same blocks of molybdenum, tungsten and isotropic graphite, in order to limit potential inhomogeneity effect, according to the requirements of each partner in terms of dimensions and geometry. The results obtained on these homogeneous solid materials will be made available on a repository and can be downloaded and reused by end-users in academic and industrial communities.

After these inter-laboratory comparisons, the partners will characterize the thermophysical properties (thermal diffusivity, specific heat and emissivity) at very high temperature of “industrial” materials (composites and metallic alloys) which will be provided by the industrial partners involved in the project or in the stakeholder advisory board.

Establishment of methods for quantifying de-bonding at high temperature (above 1000 °C)

A laser flash set-up has been adapted to measure the thermal contact resistance in multilayer systems from the temperature measurements of the front side and back side on the tested specimen. A numerical model based on control volume method, which predicts the temperature field development versus time during these laser flash experiments, has been developed and validated. Measurements on samples with dedicated defects have been performed with another set-up (based on thermal imaging measurements) to find a validated approach for detection of mechanical de-bonding.

A report presenting the feasibility of making relevant multilayers for the project and proposing potential multilayers systems has been prepared. The development and characterization of bi-layer and tri-layer systems and of partially de-bonded bi-layer and tri-layer systems is in progress. The initial tests of potential candidate multi-layered material systems have been carried out on 4 systems: SiC-China clay-Mullite, Al_2O_3-glass ceramic, Si_3N_4-Pyroceram-Si_3N_4, and Al_2O_3-Al foil-Al_2O_3. Based on these initial tests, the SiC-China clay-Mullite has been recommended for detailed characterisation.

Laser flash tests have been thus performed on bi-layer and tri-layer samples of SiC-China clay-Mullite systems at room temperature and their interface conductance (without partial de-bonding) has been calculated using the inverse heat transfer model developed.

Impact

The activities and early results of the Hi-TRACE project have been presented through 13 contributions (oral presentations or posters) at national and international conferences. The project has been presented at the EURAMET Technical Committee for Thermometry which took place in Italy in April 2019. This committee is composed of the representatives of the temperature or thermophysical properties laboratories of the European National Metrological Institutes. A newsletter has been prepared in December 2019 and put on the project website and an article has been submitted in a trade journal of the nuclear energy industry.

A specific training session related to thermophysical properties measurements has been provided to young researchers coming from National Metrology Institutes (NMIs) and Designated Institutes (DIs) from Turkey, Slovakia, Greece, Bosnia & Herzegovina, Serbia, Italy during the Thermal metrology Summer School organized by Euramet TC-T end of 2018. A workshop describing the work done in the project will take place at ZAE (Würzburg - Germany) in September 2020.

To ensure the project activities remain aligned with stakeholder needs the consortium has built up a stakeholder advisory board. It is currently composed of six members, and two other potential candidates have confirmed their wish to be member.

Further to contact established with CEN TC 184 SC1 “Composite ceramics”, it has been proposed that the progress of the project Hi-TRACE would be presented during the “Forum Research and Standardization” addressed to research, industrial and scientific community in advanced technical ceramics. This event, programmed on 10th September 2020 along with the CEN/TC 184 meetings, will give an opportunity to push forward any new requirements for standardization subsequent to results obtained in the framework of the project Hi-TRACE that could be endorsed as standardization actions.

Impact on industrial and other user communities

The European community, as well as worldwide metrology and scientific communities, will benefit from reliable thermophysical properties data at high temperatures generated by a network of reference facilities. Each of the facilities will be accompanied by its uncertainty budgets, some candidate reference materials and calibration procedures. This will enable NMIs and DIs to prepare commercial offers in order to propose calibration and test services after the end of the project.

The main industrial areas that may directly benefit from project results are present in the project as stakeholders: aerospace industry, nuclear industry and manufacturers of measurement devices. They are all equipped with facilities to measure thermal diffusivity, specific heat, temperature of fusion and emissivity.

Impact on the metrology and scientific communities

Based on the project's results, a good practice guide for measurement of thermal diffusivity up to 3000 °C by laser flash method will be issued. The guide will contain information about sample requirements, measurement methodology, and analyse of the measurements to obtain the thermal diffusivity values.

Scientific results of the project will be disseminated through conference presentations, publications and training sessions. Further to this, materials for calibration of laser flash apparatus, calorimeters and emissivity devices at very high temperature will be identified.

Impact on relevant standards

The use of new matrix ceramic composite materials for nuclear applications requires thermophysical test standards to support not only material development and property databases, but design codes and component specification documents, as well as Nuclear Regulatory Commission regulations on nuclear design approval, certification, and licensing.

These standards, validated by worldwide experts will give confidence in the reliability of the thermal properties measured with these "approved" test methods and then in the design and justification files established with these values. In this project one partner is chairman of the CEN/TC 184/SC 1 "Advanced technical ceramics - ceramic composites" and member of the ISO TC206 WG4, and participates actively in the revision of standards in the field of properties measurements of ceramics.

It is planned to use the results of the project to propose new standards on emissivity measurements or update of two existing ones: ISO 19628 "Fine ceramics (advanced ceramics, advanced technical ceramics) - Thermophysical properties of ceramic composites - Determination of specific heat capacity" and ISO 19629 "Fine ceramics (advanced ceramics, advanced technical ceramics) - Thermophysical properties of ceramic composites - Determination of unidimensional thermal diffusivity by flash method".

Longer-term economic, social and environmental impacts

Compared to the usual industrial sectors (ironmaking, food, telecommunications etc.), space and nuclear industries work with long-term projects (typically 10 to 20 years). The expected long-term benefit is a full characterisation (thermal diffusivity, specific heat, emissivity, temperature of fusion) of the materials developed in this project, with quantitative uncertainties, even without a calibration certificate as far as traceability is concerned.

The aeronautics sector will benefit from using new experimental tools and models of thermal contact resistance measurements in evaluating the progress of ablation phenomena. It may contribute for example to the reduction of space module weight, the sustainability of refractories, and the extension of gas turbine lifetime thus reducing waste.

List of publications

None

<table>
<tr><td colspan="2">Project start date and duration:</td><td>01 July 2018, 36 months</td></tr>
<tr><td colspan="3">Coordinator: Bruno Hay, LNE   Tel: +33 1 30 69 12 20   E-mail: bruno.hay@lne.fr
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<tr><td>Internal Funded Partners:
1 LNE, France
2 NPL, UK
3 PTB, Germany
4 VINS, Serbia</td><td>External Funded Partners:
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