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 develop new materials able to work at higher temperatures. The overall objective of this project was to establish a European metrological infrastructure composed of reference facilities in order to provide industries with reliable and accurate thermophysical properties data for solid material up to 3000 °C.

The project has developed or has improved methods and equipment for the measurements of thermophysical properties at ultra-high temperatures, and demonstrated their metrological capabilities through the thermal characterization of several refractory materials. Reference facilities are now accessible to industry at consortium partner organisations and datasets with high temperature thermal diffusivity, specific heat, and spectral emissivity values of the materials studied during the project are available in the Zenodo open access repository.

Need

Over recent years, the operational temperatures of process plants or components in safety-critical applications have been increased, 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, for example, 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 cladding applications, 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 fibre reinforced 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 existed at very high temperatures (above 1500 °C) for assessing uncertainties of the measured values. In order to fill this gap, it was needed to have reference facilities based on absolute measurement methods with their corresponding uncertainty budgets.

Objectives

The aim of the project was 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 were:

1. To establish a reference facility based on the laser flash method for traceable measurement of thermal diffusivity of solid materials between 1500 °C and 3000 °C and to determine the related 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 was 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 was 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 operated facilities for measuring thermophysical properties of solid materials (alloys, polymers, complex coatings etc.) in order to provide industries with certified values and associated uncertainties.

Prior to this project, *specific heat* and *spectral emissivity* were measured in these institutes for temperatures lower than 1500 °C. Some reference facilities had been developed and characterised in terms of metrology up to 2000 °C for *thermal diffusivity* measurements during a previous project. At the same time, academic laboratories and instrument manufacturers had developed and extended new measurement methods up to 3000 °C. Reference facilities have been improved or developed in the Hi-TRACE project for each of these properties in order to obtain reference values for solid materials in the temperature range from 1500 °C to 3000 °C. This enables to provide traceability to measurements performed by industrial and academic users with their equipment.

Temperature of fusion of refractory materials is not among the properties routinely measured in laboratories around the world, in particular when the temperature limits of conventional high-temperature furnaces are approached or even exceeded. In view of new classes of advanced materials under development, such as ultra-high-temperature-ceramics, it was important in the frame of this project to identify methodologies to perform measurements of the temperature of fusion, with associated uncertainty budgets, and to demonstrate the challenges related to these extreme measurement conditions.

De-bonding phenomena of thermal barrier coatings applied onto turbine blades have been studied before. The existing approaches for non-contact and non-destructive techniques for quantifying the state of adhesion of such coatings by using optical or infrared radiation were not satisfactory and not validated. The project went beyond the state-of-art by providing validated measurement facilities of *thermal contact resistance*, dedicated reference artefacts and numerical tools that were 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

A reference laser flash apparatus (LFA) has been modified to operate at very high temperature by improving the inductive furnace used and by implementing new bi-chromatic radiation thermometers that have been calibrated up to 3000 °C. An in-situ calibration method of the radiation thermometers was developed by using metal-carbon eutectic high temperature fixed points 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 were designed and used to test the proposed calibration method. Cells having the same shape and size as the usual samples gave the best results in terms of uncertainty.

A comparison involving this reference facility and other commercial or homemade LFA apparatus has been organised in order to assess the variability and coherency of thermal diffusivity measurements performed at very high temperatures up to 2800 °C at the European level. Three refractory materials (molybdenum, tungsten and isotropic graphite) were used for this inter-laboratory comparison and for two others on specific heat and emissivity measurements. The specimens needed were machined in the same blocks of materials in order to reduce any potential scattering of results between partners due to inhomogeneity effects. Thermal diffusivity measurements were performed on the three materials up to the maximum temperatures that can be reached by the facilities used. The analysis of results showed a good agreement between results obtained by the participants with relative deviations above 400 °C lower than ± 4 % for molybdenum, lower than ± 5 % for IG210 graphite and up to ± 9 % for tungsten.

The uncertainties associated with thermal diffusivity measurements performed at high temperature by the laser flash method have been assessed for these three materials. It has been demonstrated that thermal diffusivity can be measured on solid refractory materials at very high temperature (up to 3000 °C in case of isotropic graphite) with a relative expanded uncertainty (k=2) lower than 5 %, if the thermal expansion of the tested material is corrected.

After these inter-laboratory comparisons, the facilities developed during the project were applied to characterize the thermal diffusivity and specific heat at very high temperature of a metallic alloy and C/SiC and SiC/SiC composite materials, provided by the industrial partners involved in the project or in the stakeholder advisory board.

The objective was successfully achieved with the development of a reference laser flash apparatus enabling to perform thermal diffusivity measurements traceable to the SI with relative expanded uncertainty (k=2) between 3 % and 5 % in the temperature range from 23 °C to 3000 °C, these new capabilities being first in the world.

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

Two drop calorimeters based on different technical solutions have been developed. In the first configuration, a heat flux calorimeter composed of two thermopiles was integrated in an isothermal block that has been positioned under an inductive furnace. In the second case, the heat flux calorimeter was replaced by a copper block equipped with thermistors, the other elements being more or less similar to the first one.

A procedure enabling the calibration in heat flux of these calorimeters by the electrical substitution technique was developed, in order to ensure the direct traceability to the SI of the specific heat measurements. Determinations of the sensitivity of the thermopiles by electrical calibration showed good linearity versus dissipated electrical energy.

A theoretical concept for dynamic specific heat measurement based on laser flash technique was proposed for samples with known spectral emissivity. It has been tested experimentally using a graphite coating deposited on tungsten samples. Additionally, a sub-second pulse-heating facility has been modified for measuring the specific heat at temperature above 1500 °C.

Specific heat measurements have been performed at very high temperature (up to 3000 °C when it was possible) on the two metallic materials (molybdenum and tungsten) by using both, drop calorimetry and pulse calorimetry techniques. Measurements were also carried out on the isotropic graphite with more difficulties, because the samples were too brittle and broke when fixed on the facilities.

The uncertainties associated with high temperature specific heat measurements have been assessed for these two metrological approaches (pulse-heating or drop calorimetry). It has been shown that the original uncertainty target of 1.5 % above 1000 °C was not reachable due to technical difficulties (e.g., temperature homogeneity of the inductive furnaces) and changes or contaminations of the specimens, and that an expanded uncertainty (k=2) of 5 % to 10 % was a more realistic value at the highest temperatures.

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, has been setup in order to enable traceable measurements of normal spectral emissivity at very high temperature. An induction heating system has been designed, manufactured and installed with dedicated sample holders made from Al_2O_3 for temperatures up to 1500 °C and from graphite and tungsten for temperatures up to 2500 °C.

Two other existing setups based on the radiometric approach were upgraded, and these systems for emissivity measurements were compared to the reference one through an inter-laboratory comparison.

The surfaces of the tungsten and molybdenum specimens received being not of uniform quality, they were sandblasted in order to improve the specimen-to-specimen variation. The improvements by sandblasting of the surface and roughness uniformity were confirmed by optical microscopy. In addition, these specimens were heated in a preliminary step to a temperature 50 K above the highest measurement temperature in order to stabilize their surface properties. Changes in surface structure were also investigated using EDX and electron microscopy, and it was observed that upon heating potential contamination on the surface was removed and the fine surface structure of the sample was smoothened.

The results of normal spectral emissivity obtained by the three participating institutes were compared in common temperature (between 1200 °C and 1800 °C) and wavelength (from 600 nm to 2 µm) ranges in order to validate the different metrological approaches applied. These results were in good agreement considering the relative deviations and the uncertainties of measurement.

An existing preliminary uncertainty budget was updated to include parameters connected with the improved reference facility. The underlying mathematical model was transferred to a Monte Carlo simulation in order to compute the measurement uncertainty from the probability distribution of influencing parameters. The achieved uncertainties ($k = 1$) were between 2.6 % and 11 % depending on the material, the temperature and the wavelength.

Three pulse-heating facilities have been improved for measuring the temperature of fusion of materials at temperatures between 1500 °C and 3000 °C.

The objective was successfully achieved even if this study concluded that the original uncertainty target of 1.5 % associated with normal spectral emissivity measurements above 1000 °C was not achievable at high temperature.

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

A laser flash set-up (LFA) has been adapted to measure the thermal contact resistance in multilayer systems from the temperature measurements of the front and back side on the tested specimen. An inverse heat transfer model, used to extract the thermal interface resistance of bi-layer and tri-layer material systems from thermograms obtained during these laser flash experiments, has been developed and validated. It has been designed to allow setting the thermal interface resistance of the de-bonded region and that of the rest of the interface area to different values.

A customised procedure has been proposed to calibrate this facility with samples of plasma-spray partially-YSZ- and alumina-coatings above 1000 °C. Furthermore, a setup for performing thermal imaging measurements has been developed and applied on layered systems. It successfully detected partial delamination underneath thermal barrier coatings.

Bi-layer and tri-layer systems (composed of IG210 graphite layers and metal foil bonds or SiC layers and Mo foil) with and without defect region at the centre have been manufactured. The quality of the bonded systems has been checked non-destructively by using a scanning acoustic microscope (SAM). The IG210 graphite/Hf foil/IG210 graphite systems theoretically had the potential to be an artefact that could be used above 2000 °C. However, using SPS process (spark plasma sintering) it was found problematic to reproducibly manufacture other batches of this artefact. The SiC/Mo/SiC systems showed excellent potential to become a high temperature LFA reference artefact.

LFA measurements have been carried out up to 1200 °C by three laboratories on the artefacts of the two material systems and the experimental curves (thermograms) were analysed by the pilot of this intercomparison. The inverse heat transfer model has been applied to calculate the interface thermal resistance, i.e. the bond quality, of these layered specimens (with and without defects) from the LFA thermograms. Measurements on samples with dedicated defects have been also performed with the set-up based on thermal imaging to find a validated approach for detection of mechanical de-bonding.

The objective was successfully achieved. The quantification of mechanical adhesion (i.e. state of bonding) was investigated using these two approaches. A software has been developed to evaluate the uncertainties associated with the bond quality parameters and heat transfer coefficients.

Impact

The activities and results of the Hi-TRACE project have been presented through 20 contributions (oral presentations or posters) at national and international conferences, as well as in eight articles published in open access scientific peer-reviewed journals. An article describing the project has been also published in a trade journal of the nuclear energy industry. Three additional papers have been written: two are non-open access and another one has been drafted. The latter one will be open access.

A one-day workshop was held online on January 2021 with about 40 attendees. The industrial needs, the main achievements and the results obtained were presented, and a virtual tour of the laboratories of the organizing partner with demonstrations was also included.

To ensure the project activities remain aligned with stakeholder needs, the consortium has built up a stakeholder advisory board composed of ten members coming from industry and scientific community. It provided feedback on the work of the consortium, the results from the project activities and gave advice on the “industrial” materials to be studied.

Impact on industrial and other user communities

The main industrial areas that may directly benefit from the outputs were involved in the project as stakeholders: aerospace and nuclear industries, and manufacturers of measurement instruments. They are all equipped with facilities to measure high temperature thermal properties and their proximity with the consortium enables an early exploitation and adoption of the outputs.

Thanks to the network of reference facilities developed during the project, the European industrial community can benefit from reliable and traceable thermophysical properties data at high temperatures. New commercial offers of calibration and test services about thermophysical properties measurements up to 3000 °C are proposed by the partners (in particular for thermal diffusivity and specific heat) and have already been applied to specific demands coming from space and metallurgy industries.

The reference laser flash apparatus improved during the project participated in a “feasibility study” to demonstrate to the European space industries and agencies its capability to measure thermal diffusivity of advanced materials at very high temperatures.

A series of five e-learning modules related to the high-temperature thermal diffusivity measurements by the laser flash method and to the assessment of associated uncertainties have been prepared for users of LFA. These tutorials are now available in the Zenodo open access repository, and on the project website.

Three refractory materials (isotropic graphite, tungsten and molybdenum) were studied via inter-laboratory comparisons on thermal diffusivity, specific heat and emissivity measurements. The results obtained during the project do not enable to finally decide if they can be potential reference materials for calibration of calorimeters and emissivity devices. In contrast, it seems that they could be proposed as candidate reference materials for thermal diffusivity measurements, provided that additional tests would be done in terms of long-term stability. Datasets with thermal diffusivity, specific heat, and spectral emissivity values of these three materials versus temperature have been uploaded in the Zenodo open access repository.

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 the laser flash method was prepared. This guide contains information about requirements on specimens and facilities, measurement methodology and data analysis in order to obtain the proper thermal diffusivity values. It has been identified by the WG Best practice of the EURAMET TC-T (Technical Committee for Thermometry) as a document that will serve as strong basis for a EURAMET guideline currently under construction on that topic. After approval, it will be made available on the EURAMET website.

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 proposal related to the organisation of an inter-laboratory comparison on thermal diffusivity measurement of high conductive materials by the laser flash method has been submitted by the Thermophysical Quantities Working Group (chaired by the coordinator of the Hi-TRACE project) of the TC-T. It was approved by TC-T in April 2021 and registered as EURAMET project 1524. Three partners are involved in this exercise, which is an essential preliminary step to propose new Calibration and Measurement Capabilities (*CMC*) in that field.

Thanks to the experience gained in this project and to a higher visibility, several partners have been contacted by new consortia to participate in two European joint research projects related to the measurement of thermal properties at very high temperatures.

Impact on relevant standards

Discussions have been initiated with relevant national and international standardization bodies on potential impacts of the project on standards dealing with “advanced ceramics”.

An informative annex about the precision of the laser flash method and the uncertainty associated with thermal diffusivity measurements has been prepared and submitted to the ISO TC206 WG7 “Monolithic ceramics - physical and thermal properties” for addition in the ISO 18755 standard “Fine ceramics (advanced ceramics, advanced technical ceramics) - Determination of thermal diffusivity of monolithic ceramics by laser flash method”. It is anticipated that the final version of the ISO 18755 standard with this annex will be examined for publication in 2022.

A discussion should be engaged in the second half of 2022 at the CEN/TC 184 SC1 “Advanced technical ceramics - Composite ceramics” to replace the current EN821-2 “Monolithic ceramics - Thermo-physical properties - Part 2: Determination of thermal diffusivity by the laser flash (or heat pulse) method” by the new version of the ISO 18755 standard.

In the near future, the outcomes of the project 17IND11 Hi-TRACE could be used for the revision of the EN ISO 19629 “Fine Ceramics (advanced ceramics, advanced technical ceramics) - Thermophysical properties of ceramic composites - Determination of unidimensional thermal diffusivity by flash method” and EN ISO 19628 “Fine Ceramics (advanced ceramics, advanced technical ceramics) - Thermophysical properties of ceramic composites - Determination of specific heat capacity” standards in 2023 and 2026.

These actions will be done via the participation of three partners of the Hi-TRACE project in the concerned standardization committees as members or chairs of subcommittees.

Longer-term economic, social and environmental impacts

Compared to the usual industrial sectors, space and nuclear industries work with long-term projects (typically 10 to 20 years), with many steps of modelling and test for optimizing their processes and devices, especially in terms of safety and reliability. The metrological facilities developed in this project enables a full characterisation (thermal diffusivity, specific heat, emissivity, temperature of fusion) of the advanced materials used in these industries in conditions close to that encountered in their real applications.

More accurate high temperature thermophysical properties data will increase the reliability of the thermal behaviour prediction of these materials in critical conditions. This will help the concerned European industries in optimizing the modelling and test steps and in reducing the corresponding costs.

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

Eber A., Pichler P. and Pottlacher G., Re-investigation of the normal spectral emissivity at 684.5 nm of solid and liquid molybdenum. *Int J Thermophys* **42,** 17 (2021). https://doi.org/10.1007/s10765-020-02769-7

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Arduini M., Manara J., Stark T., Ebert H.-P. and Hartmann J., Development and evaluation of an improved apparatus for measuring the emissivity at high temperatures, *Sensors* **21**, 6252 (2021). https://doi.org/10.3390/s21186252

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Urban D., Anhalt K., Dynamic measurement of specific heat above 1000 K. *Int J Thermophys* **43**, 77 (2022). https://doi.org/10.1007/s10765-022-03005-0

This list is also available here: https://www.euramet.org/repository/research-publications-repository-link/

Project start date and duration:	01 July 2018, 42 months	
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Internal Funded Partners: 1 LNE, France 2 NPL, UK 3 PTB, Germany 4 VINS, Serbia	External Funded Partners: 5 ArianeGroup, France 6 CEA, France 7 FHWS, Germany 8 JRC, Europe 9 TUG, Austria 10 ZAE, Germany	Unfunded Partners: 11 NETZSCH, Germany
RMG: -		