# Measurement of thermophysical properties of liquid metallic alloys in a ground- and microgravity based research program. The Thermolab Project

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*An outline of the Thermolab Project is reported with the aim of informing on the wide range of properties which are becoming available for some industrial alloys. Selected examples of experiments and properties are provided.*

**Keywords: physical metallurgy, solidification, materials characterization, property**

## INTRODUCTION

The numerical modelling of casting and solidification of metallic alloys is becoming of increased importance in industrial processing. Applications include the optimisation of production technology, resulting in a reduction of scrap rate, waste production, and energy consumption as well as the design of new and improved casting techniques for high temperature alloys with applications in power generation, transport, and the health sector [1]. In order to fully exploit the progress in the numerical modelling, reliable thermophysical property data are required as input parameters. These can be divided into properties relevant for heat transfer, fluid flow, and microstructure evolution. Due to the high chemical reactivity of many industrial alloys at high temperature, there is a pronounced lack of reliable thermophysical property data in the liquid phase.

The *ThermoLab* project is intended to alleviate this need for selected classes of alloys [2]. The approach of *ThermoLab* to this experimental challenge has a three level structure: (i) Final benchmark experiments shall be performed with a containerless electromagnetic processing device in the reduced gravity (*m*-g) environment of the International Space Station, (ii) short and intermediate duration m-g experiments such as parabolic and sounding rockets flights and, (iii) a vigorous groundbased experimental programme using containerless as well as more established thermoanalytical techniques to provide comparison values for the *m*-g experiments as well as to provide reasonable thermophysical property values to the members of the industrial project user group (PUG) throughout the duration of the project.

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The *ThermoLab* project started in August 2001 with participating scientific groups from France (CEA Grenoble), Germany (DLR Cologne, University of Ulm), Italy (IENI Genova, University of Torino), the UK (Imperial College, National Physical Laboratory), and Sweden (KTH Stockholm). The project is coordinated at the University of Ulm. An essential aspect of the project is the close collaboration with an industrial project user group, PUG, representing the major companies in the field. The PUG suggested the alloys for the project and those thermophysical properties most important to them. The alloys selected were: *Nibased* superalloys, *Ti-alloys*, *Steels* and *Cu-alloys* [3].

In order to support the rationale of the project on a broader basis, a survey was conducted among European industries to map out their need for thermophysical property values. Over 300 responses were received from about 1000 questionaires sent out, reflecting the large need of thermophysical property values in industry. A report to ESA was compiled and distributed to industries and trade organisations. Here, we show a few typical results of the survey.

The distribution of commercial interests of those companies returning the questionaire and the distribution of thermophysical properties valued of high importance are shown in Fig.s 1 and 2, respectively. According to Fig. 1, commercial interest is rather evenly distributed between foundry, casting, spray casting, secondary refining and alloy production followed by primary metal production. Regarding secondary

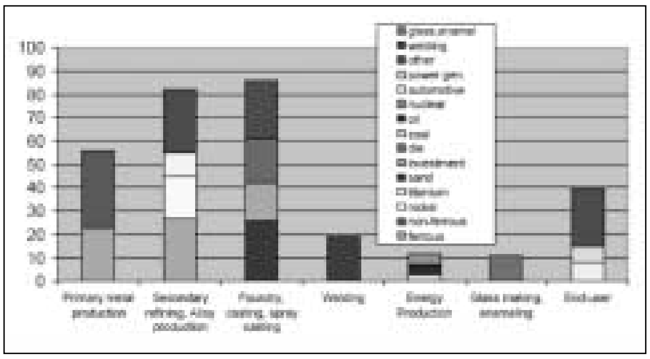

*Fig. 1 – Histogram showing the distribution of commercial interest of those returning questionnaire. Europe.*

*Fig. 1 – L'istogramma mostra la distribuzione dell'interesse commerciale dei questionari che sono stati restituiti in Europa.*

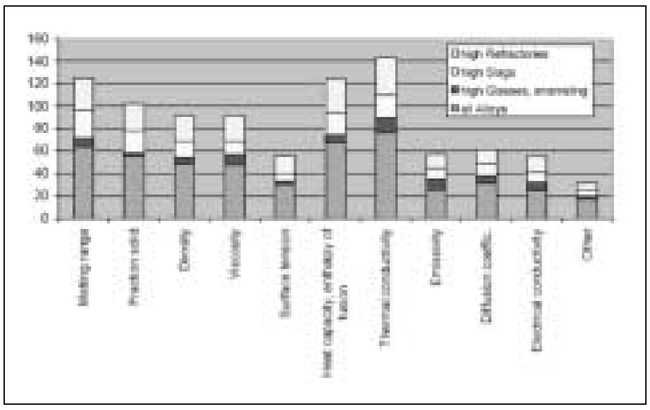

*Fig. 2 – Histogram showing the distribution of thermophysical properties with high importance according to material type. EU-all.*

*Fig. 2 – L'istogramma mostra la distribuzione delle proprietà termofisiche con importanza elevata in funzione del tipo di materiale in Europa.*

refining, the interests are almost evenly distributed between ferrous and nonferrous metals with the latter dominated by Ni- and Ti-alloys.

The distribution of properties ranked of high importance is rather similar throughout the European countries.

The distribution of thermophysical properties values suggested by the PUG members reflected very closely the distribution shown in Figure 2. The properties considered as high importance by the participating industries given as: thermal conductivity, specific heat capacity and enthalpy, melting range, fraction solid, viscosity, density, diffusion coefficients, surface tension, emissivity and electrical resistivity.

With the exception of the diffusion coefficients all properties listed can be measured within the *ThermoLab* experimental programme.

## EXPERIMENTAL

The ground-based measurement programme started with the Ni-based superalloy *CMSX-4.* It was decided that measurements should be performed in parallel at all participating laboratories in order to discern potential sources of systematic measurement error associated with different equipment and/or methods. This approach proved very useful in obtaining agreed upon thermophysical property data. An essential part of the project was the distribution of the property values such obtained to the industrial PUG.

The following measurements were performed:

- *Calorimetry*: Solidus and liquidus temperature (Torino, NPL, UUlm)
  Heat of fusion (Torino, NPL, UUlm)
  Specific heat capacity in solid and liquid phase (Torino, NPL, UUlm)
  Evaluation of the fraction solid (NPL, Torino)

An example of calorimetric traces, obtained with a high temperature differential scanning calorimetry (HTDSC), with Setaram DSC instrument, is shown in Figure 3. The cell is made of alumina and the alloy is contained in an alumina pan with some alumina powder to prevent it from sticking to the crucible walls. The sensor is a thermopile. The cell is evacuated and purged several times before measuring under flowing Helium. Sample mass was of the order of 300-400 mg. From traces show in Fig. 3a the data and solid fraction reported in Fig. 5 have been obtained [4].

On heating (Fig. 3a), there is a broad, small endothermic signal related to γ' dissolution, followed by the melting peak. At the beginning of fusion, a small signal is also observed, which can be attributed to the presence of carbides. On cooling (Fig 3b), undercooling of some degrees occurring at random as a function of heating rate is detected and a subsequent sharp peak is observed, which is indicative of crystal nucleation and dendrite growth. Moreover, on cooling the last portion of the solidification peak is probably partially overlapped to the signal due to γ' precipitation.

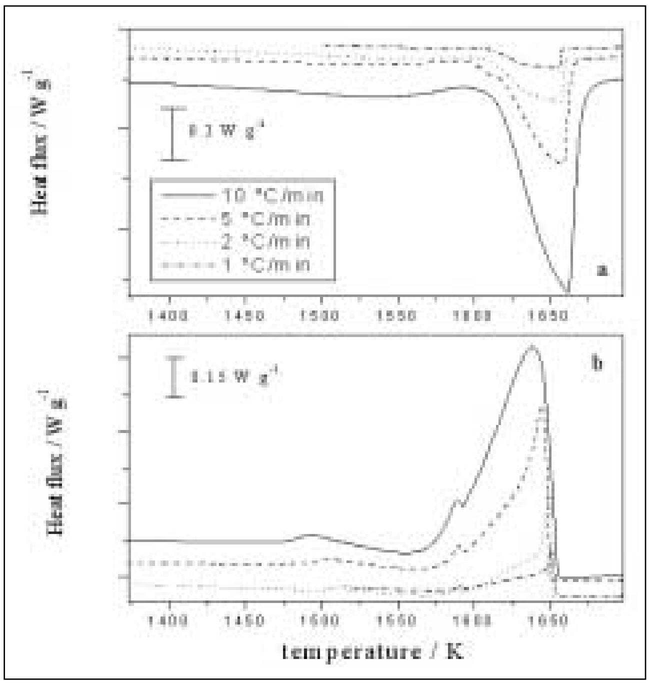

*Fig. 3 – Example of calorimetric traces: a-on heating/ b-on cooling.*

*Fig. 3 – Esempio di tracce calorimetriche: a- in riscaldamento/ b- in raffreddamento.*

- Thermal conductivity in the solid and liquid phase: Laser flash method (KTH, Netzsch)
- Density in the liquid phase: Electromagnetic levitated specimen (NPL)
- Surface tension: Sessile drop method (IENI, KTH)
  Pendent drop method (CEA)
  Oscillating drop, 1-g electromagnetic levitation (DLR)
  Oscillating drop, parabolic flight (UUlm)
- Viscosity: Oscillating cup viscosimeter (NPL)
  Oscillating drop, parabolic flight (UUlm).

In addition, a programme for the theoretical modelling of thermophysical properties was initiated and applied to the fraction solid and surface tension. An understanding of the factors influencing the compositional dependence of the surface tension, as of any other thermophysical property, is important in order to provide reasonable extrapolations of measured values to a whole range of related alloy compositions. For a proper interpretation of experimental results the effects of surface segregation and compound formation, as well as the effects of oxygen and oxygen solubility on the surface tension of industrial multicomponent alloys were investigated. The role of these effects in determining the surface tension is, in principle, well understood, however, it is only recently that they are taken into account experimentally.

## RESULTS AND DISCUSSION

Two representative results of the ground-based experimental programme are shown in Figs 4 and 5. In the figure 4 is shown the thermal diffusivity of the Ni-based superalloy *CMSX-4* in the liquid phase measured by the laser flash method under flowing Argon. To measure the thermal diffu-

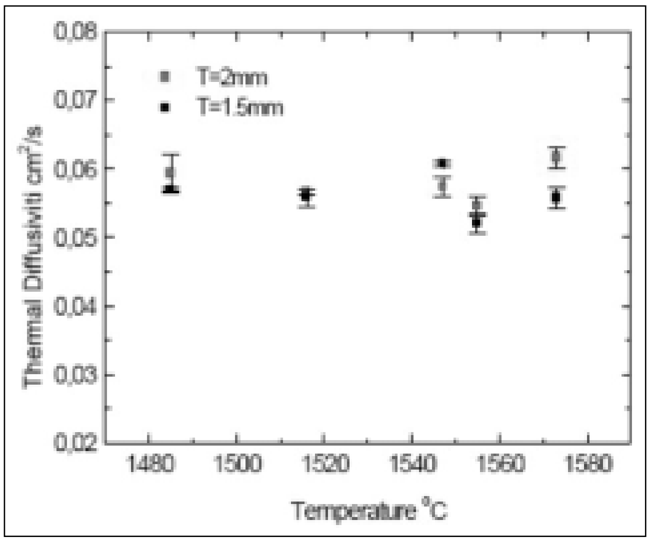

*Fig. 4 – Thermal diffusivity of CMSX-4 as a fuction of temperature in the liquid phase measured by the laser flash method. T:sample thickness.*

*Fig. 4 – Diffusività termica della CMSX-4 in funzione della temperatura nella fase liquida misurata con il metodo laser flash. T: spessore campione.*

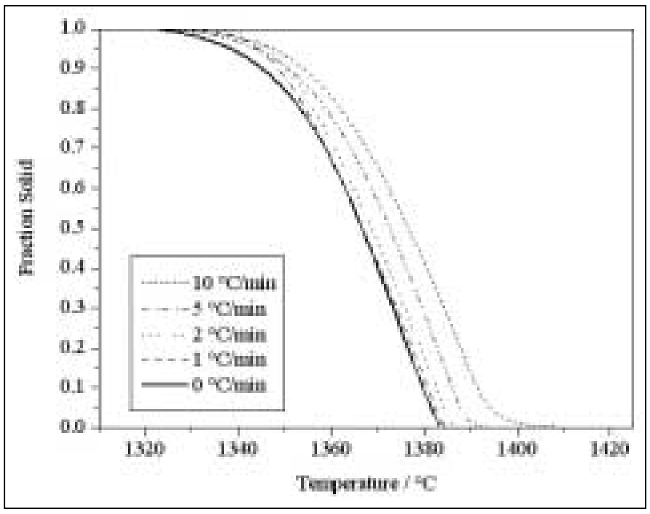

*Fig. 5 – Calorimetry: Solid Fraction traces of CMSX-4 as a fuction of temperature on heating at different rate.*

*Fig. 5 – Calorimetria: Frazione solida della CMSX-4 in funzione della temperatura riscaldando a diverse velocità.*

sivity, the upper surface of a disk-shaped specimen was irradiated with a single energy pulse from a top-mounted Nd-glass laser (2.40 kV). Immediately after the laser flashes, the temperature of the rear surface of the sample was measured as a function of time using a photovoltaic InSb infrared detector. The signal from the detector is amplified and sent to a computer for analysis. The thermal diffusivity $\alpha$ can be calculated by the following Eq. (1):

$$\alpha = 1.37L^2 / \pi^2 t_{1/2}$$

where $L$ is the thickness of the sample and $t_{1/2}$ is the time required for the temperature rise of the rear surface to reach the half of the maximum temperature rise. The measurement was carried out during the cooling cycle over the temperature range between 1753 and 1853 K using the two different sample thicknesses of 1.5 and 2 mm. The measurement was repeated three times at each condition.

Solid fraction curves at different heating rates are reported in figure 5. This figure have been obtained from the traces shown before in figure 3a.The curves follows the correct temperature dependence, except a partial overlap at the beginning of melting probably due to some inhomogeneity in the specimens. The curve termed "0 °C/min" is the result of an extrapolation procedure. The temperatures at which a given solid fraction occurs at various heating rates were linearly fitted and extrapolated to zero rate. The set of temperatures obtained were then fitted using a polynomial, providing the curve reported. This procedure is suitable to determine solid fraction which cannot be measured on solidification because of undercooling [5].

For some alloys like the Ti-alloys, the full experimental programme could not be applied because of their high melting temperatures and the high chemical reactivity. These alloys have to await the space experimental programme with the application of entirely containerless processing conditions. Within the first phase, three parabolic flights organized by the European and German Space Agencies, ESA and DLR, respectively, provided the opportunity for short duration microgravity experimentation with an electromagnetic levitation device for the measurement of the surface tension and the viscosity. Parabolic flights offer a time period of 20 seconds of reduced gravity. This time is sufficient to melt, heat into the stable liquid phase, and cool a specimen to solidification. It could be demonstrated that this rather limited time slice is very well suited for the measurement of the surface tension and the viscosity.

During the typically 20 seconds of reduced gravity, a specimen can be freely suspended by a radio-frequency electromagnetic field, heated into the liquid phase where surface oscillations are excited by a magnetic field pulse, and then cooled to solidification without contact with any container walls. Processing can be either in vacuum or in a high purity gas atmosphere. For the parabolic flight experiments, an active gas cooling system was added to the facility to assure that a liquid metallic specimen can be solidified during the 20 second duration *m*-g phase. In order to increase the processing time in the liquid phase, specimen are preheated to approximately 900–1000 °C before the onset of the *m*-g phase. After having reached maximum temperature, typically 300 - 400° C above the melting point, the heater is turned off and the specimen cools freely. The time span of 12-14 seconds available in the free cooling period is sufficient for the measurement of the surface tension and the viscosity. In the free cooling period, magnetic field pulses are applied for the excitation of surface oscillations. The surface tension and the viscosity are evaluated from the frequency, and the damping time constant of the surface oscillations, respectively.

This type of processing is particularly well suited for the high-temperature alloys of this project such as *Ti-alloys* with liquidus temperatures above 1650 °C, and *Ni-based* superalloys. A large number of alloys has been processed: *Ti-alloys* including *g -TiAl* provided by *Ladish*, *TIMET* and *MTU*, *Ni-based* superalloys provided by *DONCASTERS*, *ALSTOM Switzerland* and *MTU*, an *Fe-alloy* provided by *CORUS*, and *cast irons* provided by *DaimlerChrysler*.

The evaluation of the surface tension from the surface oscillation frequency is well established and provided valuable data while the evaluation of precise viscosity values requires some improvement in the experimental methodology. As such, surface tension measurements under reduced gravity conditions in a parabolic flight can serve to verify results obtained in ground-based laboratory.

In Fig. 6, a typical processing sequence from a parabolic flight is shown for the *Ti6Al4V* alloy with (1) melting, (2) overheat, (3) free cooling after the heating field has been turned off and the excitation of surface oscillations, and (4) undercooling with recalescence. As a result, in Fig. 7 the surface tension as a function of the temperature is shown.

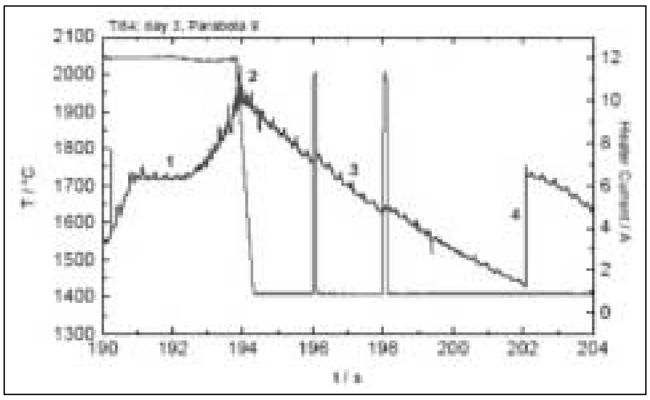

*Fig. 6 – Temperature-time profile of a Ti6Al4V specimen. Temperature shown on the left hand ordinate (black), the rf-heater oscillating circuit current shown on the right hand ordinate (gray).*

*Fig. 6 – Profilo tempo-temperatura per il campione Ti6Al4V. La temperatura è mostrata sull'ordinata sinistra (nero), la corrente del circuito oscillante per riscaldamento a radiofrequenza è mostrato sull'ordinata destra (grigio).*

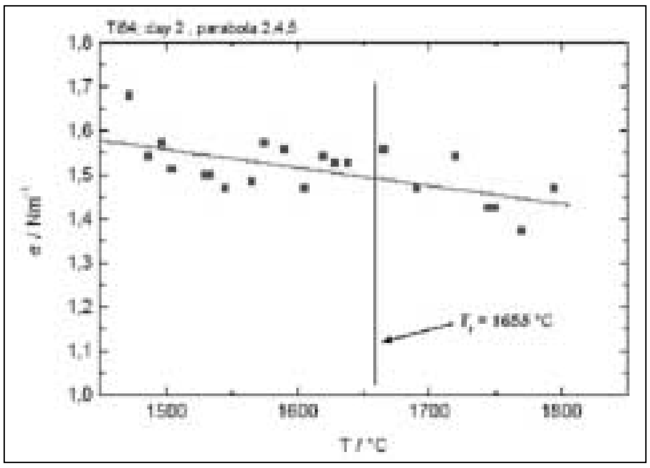

*Fig. 7 – Surface tension of Ti6Al4V as a function of temperature evaluated from three parabolas.*

*Fig. 7 – Tensione superficiale di Ti6Al4V in funzione della temperatura analizzata nel corso di tre parabole.*

Another important aspect of the project was publicity to make it known to the relevant industries and trade organisations at large. This was and is attempted by the distribution of three ThermoLab newsletters to over 200 industries and trade organisations describing the scope of the project and its progress.

## ACKNOWLEDGEMENTS

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## REFERENCES

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[2] Thermolab Final Report 2003, ESA MAP Contract Number AO-99-022.

[3] The project has now been renewed also with additional PUG members (Teksid and CSM in Italy). Participation as PUG members is open to industries willing to apply. Further information and the newsletter can be obtained from the participants.

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# ABSTRACT

## MISURA DELLE PROPRIETA' TERMOFISICHE DI LEGHE METALLICHE LIQUIDE IN ESPERIMENTI A TERRA ED IN MICRO-GRAVITA' - IL PROGETTO THERMOLAB

**Parole chiave: metallurgia fisica, solidificazione, caratterizzazione materiali, proprietà**

*Questo lavoro è stato realizzato nell'ambito del progetto ESA-Thermolab "Dati di elevata precisione per le proprietà termofisiche dei metalli liquidi per la modellizzazione della solidificazione nei processi industriali". Negli ultimi anni sono stati sviluppati software per la descrizione dei processi di riempimento delle forme e di raffreddamento delle leghe [1]. Questi software necessitano di parametri termofisici di input e questo progetto si propone di ottenere nuovi dati per leghe di formulazione industriale. A causa dell'alta reattività chimica ed alla alta temperatura di uso di molte leghe industriali, c'è un evidente bisogno di dati attendibili sulle proprietà termofisiche della fase liquida. Il progetto Thermolab intende colmare questo bisogno per delle leghe selezionate [2].*

*Il progetto Thermolab è articolato in tre livelli: (i) esperimenti condotti riducendo la forza di gravità sulla stazione spaziale internazionale, (ii) brevi esperimenti in assenza di gravità con voli parabolici, (iii) una gran quantità di esperimenti a terra. Il progetto Thermolab è iniziato nell'agosto del 2001 con la partecipazione di gruppi scientifici dalla Francia (CEA Grenoble), Germania (DLR Cologne, University of Ulm), Italia (IENI Genova, University of Torino), Regno Unito (Imperial College, National Physical Laboratory), e Svezia (KTH Stockholm). Il progetto è coordinato dall'Università di Ulm. Un aspetto essenziale del progetto, è la stretta collaborazione con le industrie che partecipano al progetto (Project User Group), le quali hanno suggerito le leghe e le proprietà termofisiche da studiare. Le leghe selezionate sono: una superlega a base Ni, leghe di Ti, acciai, ghise e leghe di Cu [3]. La distribuzione degli interessi commerciali e le proprietà termofisiche sono state determinate tramite un'indagine fatta tra le industrie potenzialmente interessate al progetto.*

*I risultati sono mostrati rispettivamente nelle figure 1 e 2. Con l'eccezione dei coefficenti di diffusione, tutte le proprietà elencate nelle figure possono essere misurate nell'ambito del progetto ThermoLab. Il programma a terra è cominciato con la misura delle proprietà termofisiche della superlega a base Ni CMSX-4.*

*Misure realizzate parallelamente da tutti i laboratori partecipanti al progetto sono servite a determinare le potenziali fonti di errore di misura sistematico connessi con attrezzature e/o metodi differenti. Un esempio di tracce calorimetriche è mostrato in figura 3 in riscaldamento ed in raffreddamento [4]. Inoltre, è stato intrapreso un programma per la modellizzazione teorica delle proprietà termofisiche ed è stato applicato alla frazione solida e alla tensione superficiale. Due risultati rappresentativi del programma sperimentale a terra sono indicati in Fig. 4 e 5. Nella figura 4 è mostrata la diffusività termica nella fase liquida della superlega CMSX-4, misurata con il metodo laser flash. Le curve della frazione solida a diverse velocità di riscaldamento sono mostrate nella figura 5.*

*La curva chiamata "0 °C/min" è il risultato di una procedura di estrapolazione [5]. Per alcune leghe come le leghe di Ti, il programma sperimentale completo non può essere applicato a causa delle loro alte temperature di fusione e di reattività chimica. A queste leghe viene applicato il programma sperimentale in assenza di gravità con voli parabolici, per la misura della tensione superficiale e viscosità. I voli parabolici offrono un periodo di tempo di 20 secondi di gravità ridotta. Questa periodo è sufficiente perché si possa fondere il campione, lo si riscaldi nella fase liquida e si raffreddi fino alla solidificazione. Questo tipo di elaborazione è adatto soprattutto per le leghe di Ti (temperature di liquidus superiore ai °C 1650). Nella Fig. 6, una sequenza tipica ottenuta da un volo parabolico è indicata per la lega di Ti6Al4V: (1) fusione, (2) riscaldamento, (3) raffreddamento libero, (4) recalescenza e sottoraffreddamento.*

*Nella Fig. 7, è mostrata la tensione superficiale in funzione della temperatura. Un altro aspetto importante del progetto è quello di essere pubblicizzato in modo da essere conosciuto nel suo insieme dalle industrie e organizzazioni commerciali interessate. Questo è stato fatto tramite la distribuzione di bollettini Thermolab che illustrano gli obiettivi ed il progredire del progetto ad oltre 200 industrie ed alle organizzazioni commerciali.*