High accuracy infrared emissivity between 50 and 1000 ºC for solar materials characterization

Raquel Fuente[1*], *Telmo* Echániz[1], *Iñigo* González de Arrieta[2], *Irene* Urcelay-Olabarria[2], *Josu M* Igartua[2], *Manuel J*. Tello[3], *Gabriel A*. López[2]

[1]Faculty of Engineering, University of the Basque Country UPV/EHU, Plaza Ingeniero Torres Quevedo,1.Bilbao, 48013, Spain.
[2]Applied Physics II, University of the Basque Country UPV/EHU, Leioa, 48940, Spain.
[3]Condensed Matter Physics, University of the Basque Country UPV/EHU, Leioa, 48940, Spain.

Abstract. The total hemispherical emissivity of materials used in the solar energy industry is a critical parameter in the calculation of the radiative thermal losses and material efficiency, especially in solar thermal collector absorbing surfaces. This is because the radiative heat losses have a significant economic impact on the final cost of the electricity produced in solar plants. Our laboratory, HAIRL, in the University of the Basque Country (UPV/EHU) in Spain [1] is the first to have published infrared spectral emissivity measurements in Solar Absorber Surfaces (SAS) at working temperature [2]. The laboratory allows measuring between 50 and 1000 ºC in the 0.83-25 μm range and is also capable of doing directional measurements at different angles between 0 and 80 degrees. Therefore, it is suitable for measuring solar selective coatings, for studying high temperature stability and for characterizing thermal energy harvesting materials. In this presentation, we show the specifications of our laboratory, the results of spectral emissivity measurements in air-resistant solar selective coatings and in eutectic alloys for thermal storage and we demonstrate the necessity of measuring at working temperature in order to possess reliable data.

1 Introduction

In the current society, where the energy demand is continuously increasing, the development of renewable energy sources is one of the challenges to face traditional resources depletion. In that sense, solar thermal energy is one of the most promising sources, with Concentrated Solar Power (CSP) experiencing a large increase in last years. Nevertheless, efforts need to be made still in improving the technology efficiency, both in energy harvesting and in storage fields.

Related to energy harvesting, it is acknowledged that conversion efficiency might be improved by a rise in the working temperature. In those systems, the solar absorber surface (SAS) is one of the most important components. A surface that facilitates the conversion of solar radiation into useful heat should possess two important properties: first, it should absorb the incoming solar radiation as much as possible (i.e. high solar absorptivity at the vis-NIR wavelengths) and second, at the same time, it should retain the collected heat (high thermal reflectivity, or low emissivity, at the NIR-MIR region) [3]. However, there is still a challenge in developing efficient selective coatings stable at such working temperatures [4-12].

Emissivity is a radiative property of materials that shows how much radiation is emitted by a given body as compared to a blackbody (perfect emitter) at the same temperature. It describes the capability of a real material surface to emit electromagnetic radiation, mainly in the infrared part of the spectrum. Complete knowledge of the emissivity values is required for many technological applications, being of key importance the data acquired at working temperatures, which are scarce in the literature (frequently extrapolated from room temperature data [13]). In the particular case of the solar energy industry, the total hemispherical emissivity of materials is identified as a critical parameter in the calculation of the radiative thermal losses and material efficiency.

Besides, until now the current storage technology in both industrial heat recovery and CSP plants has been based on sensible heat storage, using binary or ternary mixtures of simple inorganic salts. It is well known that an alternative to sensible heat storage is the use of phase change materials (PCM) [14-17]. Potential candidates for PCM with a solid-liquid phase-transition have been proposed and in some cases studied in the literature; among them, inorganic salts, paraffins, hydrated salts and fatty acids [14,15,18]. Compared to all these materials, the eutectic alloys, in addition to their high energy density, their constant heat supply and their recovery temperature, have the further advantage of a high thermal conductivity. The main structural and thermophysical properties of these eutectic alloys (melting point, specific heat, thermal conductivity, latent heat, etc.) can be found in the literature [19]. In this regard, it is known that in energy harvesting modeling,

---

* Corresponding author: raquel.fuente@ehu.eus

heat exchange by radiation needs to be considered. Therefore, the detailed knowledge of all the parameters related to the radiative heat transfer, among them the thermal emissivity, becomes very important.

Concerning the characterization of the radiative properties, the precise determination of the emissivity is decisive. For these measurements, the high accuracy radiometer of the University of the Basque Country (UPV/EHU), which allows for spectral directional emissivity measurements as a function of temperature, is selected [1].

In this work we show the specifications of the laboratory, the results of spectral emissivity measurements in solar selective absorbers together with the oxidation dynamic study for stability purposes and the characterization of radiative properties of alloys for thermal energy storage. Furthermore, we demonstrate the necessity of measuring at working temperature in order to possess reliable data.

2 Theoretical background

As it has been mentioned before, emissivity (ε) is a parameter governing thermal transport by radiation. Traditionally, it has been determined by indirect reflectivity measurements at ambient temperature and, then, extrapolated to the working temperatures [13], but here, a direct measurement is proposed. Below, three issues are presented to show the influence of an accurate measurement and control of the emissivity on the efficiency in the solar energy field.

2.1 Total hemispherical emissivity at working temperatures

It is worth noting that at CSP working temperatures, most of the heat losses occur by radiation, as they are proportional to the fourth power of the temperature. Besides, in the majority of current solar thermal collectors, the SAS is inside a vacuum chamber in order to preserve material stability at such high temperatures, but it nevertheless cannot avoid radiation heat losses. Therefore, it becomes essential for efficiency purposes to study the spectral emissivity values as a function of temperature.

It is acknowledged that Planck's Law defines the spectral radiation emitted by a blackbody as a function of temperature. One of the current methodologies for the emissivity determination follows Equation 1:

$$\varepsilon_T(T) = \frac{\int_0^\infty [1 - R(\lambda)] L(\lambda, T) d\lambda}{\int_0^\infty L(\lambda, T) d\lambda} \quad (1)$$

where L is the Planck's blackbody spectrum and R, the sample's reflectivity. It should be noted that the considered reflectivity is only wavelength-dependent. In other words, the methodology proposes a measurement, at room temperature, of the spectral reflectivity, then followed by its extrapolation, through Planck's Law, to the emissivity at any temperature.

Another methodology proposes the measurement by a commercial emissometer at a temperature of about 100 ºC and considers it constant at any other higher or lower temperature. [20]

Nevertheless, our group experience in radiative properties of materials suggests the need to substitute the approximation in Equation 1 by the real value in Equation 2.

$$\varepsilon_T(\theta, T) = \frac{\int_0^\infty \varepsilon_\lambda(\lambda, \theta, T) L(\lambda, T) d\lambda}{\int_0^\infty L(\lambda, T) d\lambda} \quad (2)$$

where ε_λ is the spectral directional emissivity.

That way, correct values of spectral emissivity measured at working temperatures are used to retrieve the total emissivity.

It should be noted that the equations presented before account for total emissivity values, although they are usually measured at a normal direction. It is clear that it can be considered a valid approximation for most industrial cases, but if a high accurate emissivity value is required, the hemispherical emissivity in Equation 3 should be considered.

$$\varepsilon_H(T) = \frac{1}{\pi} \int_0^{2\pi} \int_0^{\pi/2} \varepsilon_T(\theta, T) \cos\theta \sin\theta \, d\theta \, d\phi \quad (3)$$

2.2 Oxidation dynamics

Emissivity measurement is not only a useful property to evaluate radiation heat losses, but also allows to determinate anomalous optical or thermal behaviors at working temperatures. That is the case of thermal stability. It is usual for coatings to suffer from corrosion, and therefore they need to be under vacuum. Besides, there is a growing interest in developing stable coatings, both in air and in temperature. The emissivity allows the study of the oxidation dynamics at working temperatures [20,21].

2.3 Phase transition characterization for thermal energy storage

As mentioned before, eutectic metal alloys are recently considered a substitute to molten salts in thermal energy storage at high temperatures. The objective there is to measure the radiative properties, in particular spectral emissivity, between 200 ºC and the melting temperature, in order to characterize the solid-solid transitions and the radiation enthalpy related to them in order to account for heat losses.

3 Experimental setup

High accuracy infrared emissivity measurements are planned on various materials in the solar field: coatings and PCMs for thermal energy storage. Measurements are performed at working temperatures, 200 to 600 ºC, in order to compare the extrapolated and actually measured

emissivity values. The oxidation dynamics and the solid-solid phase transition in a PCM are also studied.

3.1 HAIRL radiometer

Our laboratory in the University of the Basque Country (UPV/EHU) developed a few years ago a hand-made radiometer to measure directly the emissivity at high temperatures [1]. The set up, sketched in Figure 1, allows measuring between 50 and 1000 degrees Celsius in the 0.83-25 μm range and is also capable of doing directional measurements at different angles between 0 and 80 degrees. The samples are heated by radiation and can be measured in vacuum, air or any controlled atmospheres.
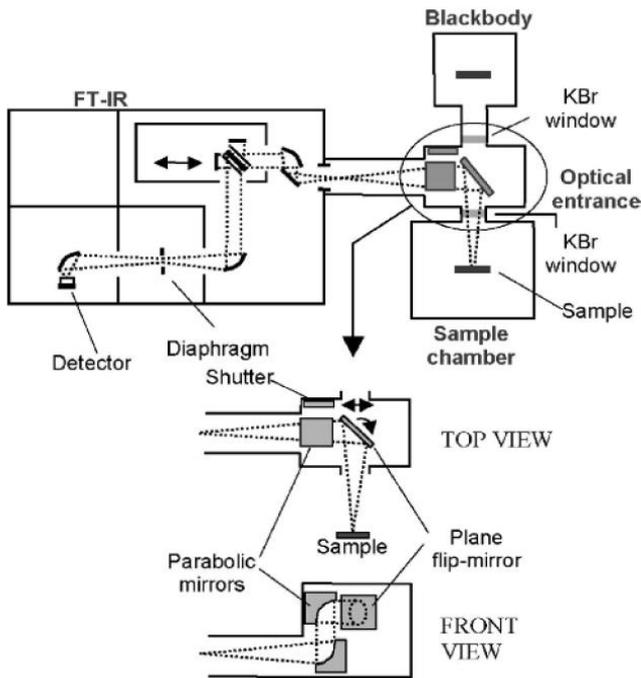

Fig. 1. Scheme of the HAIRL radiometer

3.2 Samples

Two experimental coatings have been selected for the study. The structure of the samples is schematized in Figure 2. They are typical cermet coatings, consisting of small transition metal particles embedded in a dielectric matrix deposited on a highly infrared reflecting substrate. The first sample, Figure 2 (a), is a silicon nitride based coating stable until 600 ºC [22], while the second sample, Figure 2 (b), is an aluminium oxide based coating, specially designed to be air resistant and stable until 500 ºC [23].

As it has been mentioned, both coatings have been designed for a working temperature range of 400 to 600 ºC. Therefore, a emissivity study in this range is performed for both. In addition to a reliable emissivity value, the oxidation dynamics is analyzed for the first coating, while the influence of the total hemispherical emissivity is shown for the second sample.
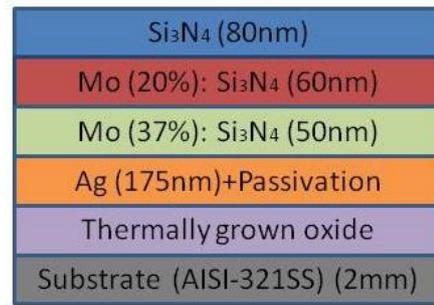
a)   Silicon nitride based coating (CSIC) [22]
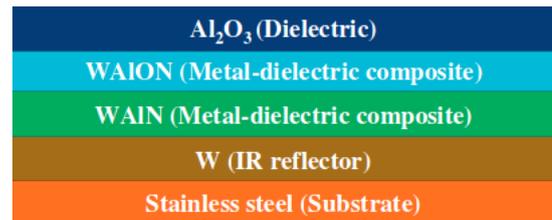
b) Aluminium oxide based coating (CSIR) [23]

Fig. 2. Structure of the solar energy selective coatings

With regard to the PCM for thermal energy storage, a monotectoid transition in Zn-3%Mg-4%Al alloy is studied [19]. It presents a reaction around 280ºC, 60ºC below the melting point, which allows studying the hysteresis cycles in the infrared emission spectrum to observe the phase transition.

4 Results and discussion

The silicon nitride based cermet coating has been studied first. In order to see the change in the spectral emissivity due to the coating, both the AISI substrate and the coating have been measured at the working temperature of 600 ºC. Figure 3 a) shows the effect of the coating: higher emission at short wavelengths and lower at long ones. Ideally, the coating should maximize absorption in the visible range and minimize emission in the infrared range. In this case, it is observed that the change of behavior with respect to the substrate occurs at around 5 μm, which results, in fact, quite far in wavelenght, since the Planck function has its maximum radiation at 400-600ºC at 3.5-5 μm.

In Figure 3 b), the total emissivity of the sample is depicted as a function of temperature in the working temperature range. First, the approximation in Equation 1 is made (red) to extrapolate the ambient results to a temperature dependent emissivity value. Then, real emissivity values are measured for both the substrate (green) and the full coating (blue) and plotted together for comparison. The first conclusion is that the extrapolation usually made for the determination of the emissivity at high temperatures gives rise to values far from the actual experimental values, provided that the emissivity of the sample is temperature dependent. Besides, it can be observed that the performance of the substrate and the coating changes at around 400ºC, so it is important to measure at the working temperature

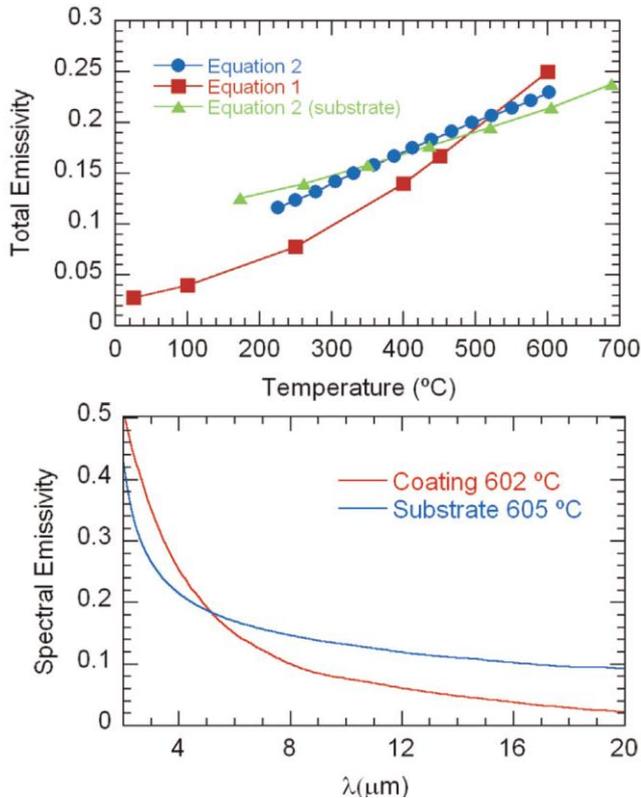range, otherwise it could lead to conclude a wrong coating efficiency.

Fig. 3. Emissivity of the cermet coating: a) Comparison of the spectral emissivity of the AISI-321SS substrate and the full cermet coating at around 600 ºC; b) Total emissivity as a function of temperature for the substrate (green) and the cermet coating, calculated using the approximation (red) and the real value (blue). [2]

In addition to the determination of the emissivity value, the oxidation dynamics has been also analyzed in order to guarantee the stability. As it has been studied before, an oxidation semitransparent layer produces interferential maxima and minima, variable as the thickness increases [24]. Figure 4 shows the spectral emissivity curves of the AISI substrate at the working temperature (600ºC) in subsequent measurements in air along a day. It can be observed that the emissivity is doubled in the range of maximum emission at this temperature (3.5-5 µm). Also, it is clearly seen the wave behavior caused by the interferences produced in the oxide semitransparent layer growing at the surface.

Besides, the aluminium oxide based coating has been studied. The total emissivity has been calculated by integrating the directional emissivity values measured from 10 to 80º, also as a function of temperature, as suggested in other studies [25]. It is worth noting that the angular dependence of the emissivity may vary due to the configuration of the multilayers. Figure 5 shows the usual normal emissivity measured, together with the hemispherical integrated value, as suggested by Equation 3. The significant difference when emission in all directions is accounted, instead of only the normal one, is clearly observed.
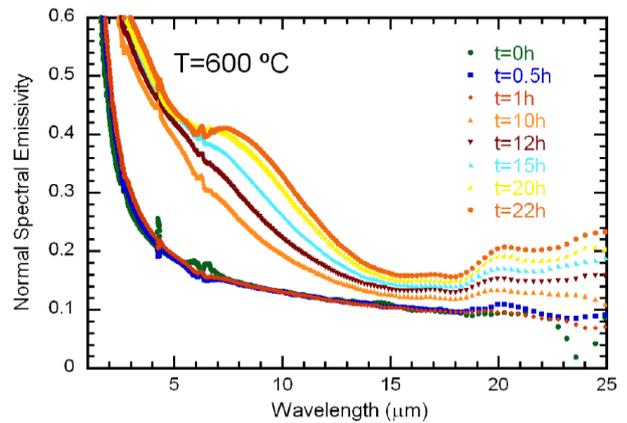

Fig. 4. AISI-321SS substrate spectral emissivity evolution during an oxidation process of 22 hours at 600 ºC in air. [20]
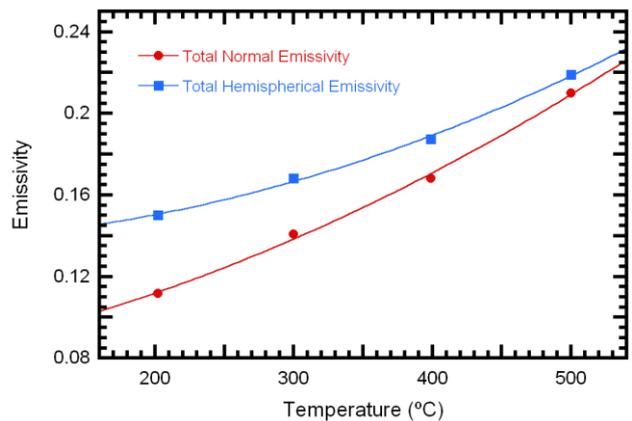

Fig. 5. Total Normal emissivity (red) and Total Hemispherical emissivity (blue) as a function of temperature for the metal-dielectric coating.
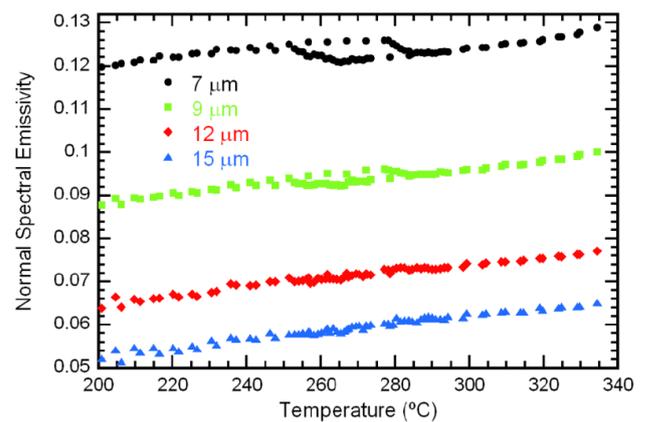

Fig. 6. Spectral emissivity of the Zn-3%Mg-4%Al alloy at four wavelengths, for heating and cooling processes.

Finally, regarding the thermal energy storage, the hysteresis cycles in emissivity around the monotectoid transition of the Zn-3%Mg-4%Al alloy are represented in Figure 6 in order to observe the phase transition. There, the normal spectral emissivity results measured during heating and cooling cycles are plotted as a function of temperature. It can be observed a difference

in the evolution of emissivity at different wavelengths. The hysteresis cycle is clearly observed at short wavelengths (7 µm), where the phase transition is detected around 280 ºC when it is heating up and around 260 ºC when it is cooling down. However, it fades as the wavelength increases, not being detected from 15 µm and longer wavelength values. The existence of this spectral threshold suggests that this emissivity variation is related to interband transitions, similar to the results observed in other optical measurements [26].

5 Conclusions

Direct measurements of spectral emissivity have been performed at the working temperatures of CSP systems, 200 to 600ºC, in various solar energy materials.

First, two cermet solar selective coatings have been characterized: a silicon nitride based coating and an aluminium oxide based coating. The first one shows the effect of the coating over the substrate and allows to accurately determine the emissivity selectivity of the coating. What is more, it reveals the effect of a direct measurement at working temperature compared to the extrapolations from room temperature that are usually performed. Also, the oxidation dynamics of the substrate have been studied through emissivity. The second coating serves to confirm the influence of the directional emissivity measurements as opposed to the usual normal ones, and therefore, establishes the necessity to determine and use the total hemispherical emissivity as the accurate emissivity reference value.

With regard to the thermal energy storage, the spectral and total normal emissivities of a PCM alloy, Zn-3%Mg-4%Al, have been determined as a function of temperature in solid state. This allows the characterization of the phase-transition through emissivity measurements, which in turn show the precision of the radiometer and the performance when dealing with slight emissivity changes.

In brief, we demonstrate the necessity of direct emissivity measurements at working temperature to accurately characterize heat transfer processes.

References

1. L. del Campo, R.B. Pérez-Sáez, et al,. Review on Scientific Instruments **77** (2006)113111.

2. T. Echániz, I. Setién-Fernández, et al, Solar Energy Materials&Solar Cells 1**40** (2015)249.

3. C.E. Kennedy, *Review of mid-to-high-temperature solar selective absorber materials*, NREL/TP-520-31267.

4. C.G. Granqvist, Solar Energy Materials & Solar Cells **91** (2007) 1529-1598.

5. G.A. Niklasson, C.G.Granqvist, J.Mater.Sci. **18** (1983) 3475–3534.

6. N. Selvakumar, H.C.Barshilia., Sol. Energy Mater. Sol.Cells **98** (2012)1–23.

7. F.Cao, K.McEnaney, G.Chen, Z.Ren, Energy Environ. Sci. **7** (2014)1615–1627.

8. H. Tabor, Bull. Res .Counc. Isr. 5A (1956) 119.

9. B.O. Seraphin,et al, in: B.O.Seraphin (Ed.), *Optical Properties of Solids- New Developments,* North-Holland,Amsterdam,1976,p.927(Chap17).

10. R.E. Hahn, et al, Phys.ThinFilms **10**(1978)1–69.

11. A.J.Sievers, in :B.O.Seraphin(Ed.), *Solar Energy Conversion: Solid State Physics Aspects*, Springer, Berlin, Heidelberg,1979,p.57.

12. C.M. Lampert, Sol. Energy Mater. **1** (1979) 319.

13. *'Standard Test Method for Solar Absorptance, Reflectance, and Transmittance of Materials Using Integrating Spheres'* (E903-12), ASTM standard, Technical report.

14. B. Zalba, J.M. Marin, et al., Applied Thermal Engineering **23** (2003) 251–283.

15. M.M. Kenisarin., Renewable & Sustainable Energy Reviews **14** (2010) 955-970.

16. M. Liu, et al, Renewable & Sustainable Energy Reviews **16** (2012) 2118-2132.

17. A. Gil, M. Medrano, et al, Renewable & Sustainable Energy Reviews **14** (2010) 31-55.

18. X. Meng, H. Zhang, et al, ., Journal of Thermal Analysis and Calorimetry.**111** (2013) 377-84.

19. E. Risueño et al. Energy Procedia **69**(2015)1006.

20. I. Setién-Fernández, T.Echániz, et al., Sol. Energy Mater. Sol. Cells **117**(2013) 390–395.

21. L.del Campo, et al. International Journal of Thermophysics **27** (2006) 1160–1172.

22. E. Céspedes, M. Wirz, et al., Solar Energy Materials & Solar Cells **122** (2014) 217-225.

23. A. Dan et al., Thin Solid Films **620**(2016)17.

24. L. del Campo, R.B. Pérez-Sáez, M.J. Tello, Corrosion Science **50** (2008) 194-199.

25. A. Dan, B. Basu, T. Echániz, et al., Sol. Energy Mater. Sol. Cells, **185**, 342 - 350 (2018)

26. V. Saidl, et al, New. J. Phys. **18** (2016) 083017.