

# COMPLEX OXIDE STRUCTURES AS AN ALTERNATIVE SOLUTION FOR HIGH TEMPERATURE COATINGS

E. Y. Sako<sup>1</sup>, H. D. Orsolini<sup>1</sup>, D. Galesi<sup>1</sup>, M. Moreira<sup>2</sup>, V. C. Pandolfelli<sup>2</sup>

<sup>1</sup> Saint-Gobain Performance Ceramics and Refractories, Vinhedo-SP, Brazil

<sup>2</sup> Federal University of Sao Carlos, Materials Microstructure Engineering Group, São Carlos-SP, Brazil.

## ABSTRACT

High-emissivity coatings have been pointed as a promising energy saving solution for industrial furnaces since their development in the aerospace market. However, due to a lack of deep knowledge on radiation heat transfer and thermal-optical interactions as well as the struggle in obtaining proper emissivity values, commercial versions of such coatings have not been widely established yet. In this work, an extensive evaluation of the fundamentals on the physics of solids and thermal-optical properties led to the development of engineered structures of common oxides, such as magnesium-aluminate spinel and titanium oxide, which presented improved emissivity values, even at high temperatures, when compared to commercial references. Besides the reliable optical property measurements, an efficiency test in lab-scale was also performed to confirm the actual benefits of coatings containing the investigated compounds. The complex structures presented emissivity values twice higher than the references, pointing out an interesting saving potential for large industrial furnaces.

## INTRODUCTION

High-temperature processes are always a matter of concern related to energy loss through refractory linings. According to the literature addressing heat flow diagrams, an average of 50% of the gross fuel input in regular gas-fired furnaces for heat treatment is lost during the entire heating cycle<sup>1,2</sup>. Inspired by the success of preventing space shuttles from being greatly damaged by the heat generated during re-entry into the Earth's atmosphere<sup>3,4</sup>, the idea of using high emissivity coatings on traditional refractory linings of industrial furnace walls started to gain momentum over the two past decades. Such coatings comprise a thin layer of a very specific material (or combination of

materials) which can absorb a large amount of heat and re-emit it almost entirely back to the environment.

Despite innumerable positive results obtained by different research groups<sup>5-8</sup>, using high emissivity coatings were not as promising as expected when considering industrial applications. This is most likely because high- temperature emissivity is not a straightforward property and its measurement requires very special equipment able to isolate any interference from other components. An additional main hurdle is associated with the coating composition. Nasa's ultimate formulation of high emissivity coating, for instance, was based on tantalum-based ceramics<sup>9</sup>, which present high costs. Other authors<sup>10</sup> reported positive results by using either cerium oxide or nickel oxide as the painting pigmentation, which may become instable at high temperatures by easily reacting with the substrate. In fact, depending on the reaction products, some of them are even considered hazardous when in contact with the human body.

Finally, it is clear that an effective coating should interact with the incoming photons in a way the re-emitted energy is maximized. When hitting an opaque material's surface, a photon is either reflected or absorbed. If the system is in thermal equilibrium, the Kirchoff law states that the amount of energy absorbed by the volume of participating material is proportional to the one re-emitted back to the atmosphere. Therefore, it is important to understand the mechanisms of radiation absorption in order to increase the efficiency of high-emissivity coatings.

In principle, ceramic materials generally do not display a significant absorption response by electronic transition as they present a large energy gap between conduction and valence bands. For this reason, only high energy electromagnetic waves would be able to interact with electrons and account for the absorption index. Nevertheless, it is possible to reduce this energy gap by doping the ceramic compound network with an ion with a different valence state. This will generate new energy states in the band gap, making it easier to excite one electron from the valence band to the conduction one and, therefore, increase the absorption of the incoming radiation.

Additionally, the material's absorptivity is increased when its lattice parameter is distorted by inserting ions with different ionic radii in the unit cell<sup>11</sup>. This behavior is associated with the increase in the network's non-harmonic vibration, favoring the re-emission of the absorbed photons. Moreover, for ions with electrons at "d" valence layer, such as titanium, the energy values required to excite their valence electron result in high optical absorption bands in the thermal radiation spectral region<sup>12,13</sup>.

The fundamentals described above make it clear that finding commercial compounds with optimized intrinsic absorptive behavior is not straightforward, mainly for high-temperature applications where the stability is also a key aspect. Nonetheless, among the most usual raw-materials used in the refractory industry, magnesium-aluminate spinel stands out as an excellent alternative for the production of high emissivity coatings by meeting most of the criteria described before<sup>14,15</sup>. Compared with other structures, the lattice parameter of spinel is considered large, favoring the accommodation of a high quantity of ions with different ionic radii<sup>15</sup>. Therefore, despite presenting low absorptive behavior in its plain and stoichiometric state, magnesium aluminate spinel could be indeed a viable high emissivity solution when doping agents are added.

Hence, the purpose of the present work is to develop and evaluate the emissivity of two groups of promising structures: complex solid solutions with regular spinel structure doped with a tetravalent ion ( $\text{Ti}^{4+}$ ), and two titanate compounds (magnesium dititanate and zirconium titanate). The analyses relied on different temperatures, 1000°C and 1500°C, in order to develop a proper and reliable pigment for the production of high-emissivity coatings that might display such optical behavior at these operating conditions.

## **MATERIALS AND METHODS**

Table I presents five different compounds, which were produced in this work with the purpose of analyzing the effects of different doping mechanisms on the emissivity values. S1 is a regular magnesium-aluminate spinel ( $\text{MgAl}_2\text{O}_4$  – 28 wt.% of MgO and 72 wt.% of  $\text{Al}_2\text{O}_3$ ), and, based on this reference, S2 and S3 were designed by adding different doping agents, carefully selected in order to maximize the lattice parameter distortion and optimize the electronic transition of their valence layers. After realizing the relevance of  $\text{Ti}^{4+}$  ion in the crystal structure of spinel, it was also decided to produce and evaluate two titanate compositions (T1 and T2), targeting to optimize the role of titanium on the absorption/emission properties. In summary, the samples can be described as below. In addition to the spinel and titanate samples, Table I also presents a commercial reference (CR) - ITC 100 HT Ceramic Coating, from ITC Coatings (Fort Worth, Texas, USA) - as a high-emissivity comparison available in the market, and an uncoated high-alumina refractory sample (AS) produced on a lab scale (95%  $\text{Al}_2\text{O}_3$  cement-bonded castable, fired at 1500°C for 5h), as the reference value of a standard heat-treatment furnace wall/substrate.

Table I – Detailed description of the samples used in this work, with their expected objective.

Sample	Description	Objective
S1	MgAl <sub>2</sub> O <sub>4</sub> <i>Regular stoichiometric magnesium-aluminate (MA) – spinel structure</i>	Reference composition
S2	Mg(Al,Ti,Mg)O <sub>4</sub> <i>Modified complex spinel structure</i>	Create lattice distortions by adding 4+ ions in the structure
S3	Mg <sub>2</sub> TiO <sub>4</sub> <i>Inverse magnesium titanate - spinel structure</i>	Inversion of Mg <sup>2+</sup> position and inclusion of a 4+ ion in the interstice of regular MA spinel structure
T1	MgTi <sub>2</sub> O <sub>5</sub> <i>Magnesium dititanate – pseudobrookite structure</i>	Increase the presence of a Ti <sup>4+</sup> ion in the interstices of the structure
T2	ZrTiO <sub>4</sub> <i>Zirconium titanate – αPbO<sub>2</sub> structure</i>	Maximize absorption by using only 4+ cations, with a random distribution in the interstices
CR	<i>High emissivity commercial reference</i>	Reference of a commercial product in the market
AS	<i>High alumina refractory substrate</i>	Sample representing an uncoated regular heat treatment furnace wall

All compositions were attained by dry mixing the right proportions of each precursor raw-materials in ball-mill equipment for 3h and sieving in a 325 mesh in order to remove any large agglomerate. The fine powder mixes were then dry pressed, without any organic binder, using a manual pneumatic press into 20x20x75 mm samples, followed by a heat treatment for 7h at 1500°C. The fired pieces were then ground in a vibratory disc mill for 10s to fine powders (<45 μm).

In order to attain whether the original spinel was indeed modified and if the new phases were formed accordingly, the samples were characterized via X-ray diffraction using a Bruker XRD 8 Advance diffractometer (Germany). The quantitative (Rietveld method) analyses of the XRD profiles were carried out using EVA and Topas software (Bruker, Germany). In this case, besides the identification and quantification of new phases (such as the different titanate phases), this technique was useful for pointing out slight dislocations of the original spinel structure's lattice parameter.

The emissivity measurements were carried out at the CEMHTI/CNRS laboratory in Orleans, France, where a novel device was developed and reported by De Sousa Meneses et al<sup>16</sup>. For this test, rectangular samples (7mm x 7mm x 3mm) of all compositions presented in Table I were prepared and compared to the results attained for a commercial reference high-emissivity coating (CR) and also for a high alumina substrate (AS). The sample's thickness was chosen in order to guarantee an opaque medium in the frequency range studied, so there would be no effect of any other material

beneath the sample. The emissivity measurements were conducted at 1000°C and 1500°C, ranging the wavelength from 1 to 10 μm [which covers the spectrum containing the photons emitted at a large range of temperature (from room temperature up to 1500°C, according to the Planck equation and Wien's law)].

## RESULTS AND DISCUSSION

The first step of this work was to evaluate whether the samples with spinel structure (S1, S2 and S3) presented differences on the crystalline parameters. The purpose here was not to calculate the lattice constants, but to compare the  $2\theta$  position of the spinel peaks in the XRD patterns. Figure 1(a) presents the X-ray diffraction patterns obtained for the three spinel samples, where the values on the top indicate the  $2\theta$  position of the spinel peaks for each composition. It can be observed that S2 and S3 presented the main peaks located correspondingly to the spinel phase S1, however with slightly displaced positions when compared to the regular alumina-magnesia spinel. The displacement of the spinel peaks points out that the addition of ions with different valence and size successfully induced a lattice parameter change of the normal spinel structure.

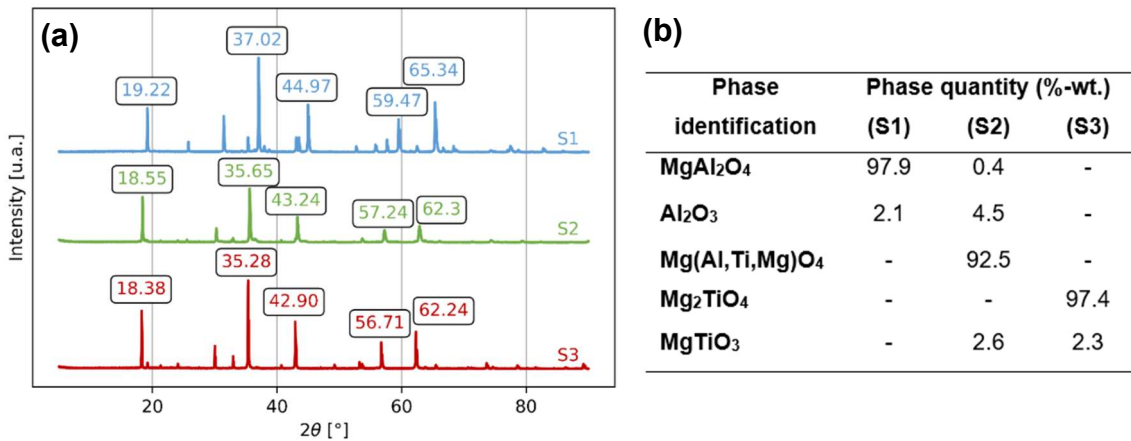


Figure 1 – (a) X- ray diffraction pattern for S1, S2 and S3 samples, highlighting the position of the main spinel crystal peaks. (b) Phase quantification of spinel-like structure samples.

The high percentage of the main spinel phases, depicted in Figure 1(b), points out that the sintering time was suitable for the reactions to properly take place. However, it was still possible to detect the presence of additional minor phases, which could also be observed by the less visible peaks which were not labeled in Figure 1(a).

After attesting the formation of the expected spinel phases, Figure 2 shows the effect of such structures on the emissivity values, which are presented as a function of both the wavenumber and the wavelength after measurements at 1000°C. The results were obtained in the range from 0 to 10000 cm<sup>-1</sup> (comprising the full spectrum of thermal radiation) for the three spinel samples and compared to the commercial reference (CR) and the regular alumina-based substrate (AS).

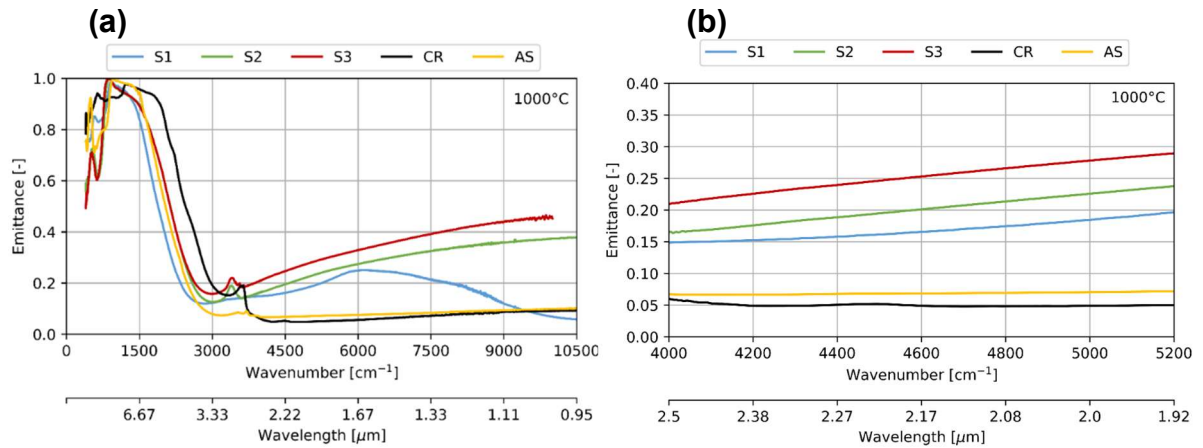


Figure 2 – Emissivity values at 1000°C as a function of the wavenumber and the wavelength for S1, S2, S3, CR and AS samples. (a) Full spectrum of thermal radiation and (b) neighborhood of the critical wavelength at 1000°C ( $\lambda_{c1000^{\circ}\text{C}} = 2.28 \mu\text{m}$ ).

Firstly, it is worth mentioning that the emissivity peak presented by some of the compounds around 3300 cm<sup>-1</sup> is related to vibrations of OH<sup>-</sup> groups which were most likely adsorbed at the samples' surface. In addition, very high emissivity values can be observed for all samples at the highest wavelength range of the spectrum. This specific effect was already analyzed by other authors<sup>17</sup> and it is denoted as “the Christiansen wavelength”, which is typical for heteropolar dielectric materials, such as alumina, spinel, carbides and nitrides. The Christiansen wavelength is defined as that ( $\lambda_{\text{Christiansen}}$ ) where the refractive index is equal to the unity and for which the extinction coefficient is enough to not induce reflection. Therefore, if the thickness of the material is high, the material's transmission goes to zero and the  $\epsilon_{\text{Christiansen}}$  is  $\sim 1$ , based on the Kirchhoff law. It is important to take this effect into consideration as it may lead to misrepresenting conclusions when evaluating high-emissivity materials. Although the samples can indeed emit electromagnetic waves like a blackbody at this characteristic wavenumber, it does not account for the spectrum region where photons emitted at actual high temperatures

(>1000°C) are included. In other words, the high emissivity behavior is only valid for the room temperature, where the critical wavelength ( $\lambda_c$ ) is close to  $\lambda_{\text{Christiansen}}$ .

In Figure 2(b), one can observe that the alumina-based substrate presented a very low emissivity value ( $\epsilon < 0.1$ ), which was already expected due to its intrinsic reflectivity behavior at this wavelength and temperature. The most surprising outcome was the very low values measured for the commercial coating sample, which points out that its high-emissivity denotation was most likely based on the values achieved at the Christiansen wavelength. Regarding the spinel samples, although they did not show significantly increased emissivity values either, it can be confirmed that the positive effects led by the modifications of their original structures. By changing the position of the cations in the octahedral and tetrahedral sites and distorting the lattice parameter, S2 and S3 showed slight improvements when compared to the S1 reference, and a much better performance than the selected commercial material.

It is also important to point out that the difference between S1 and the modified spinel versions becomes more evident as the wavelength decreases towards the final range of the spectrum, which is directly related to the presence of  $\text{Ti}^{+4}$ . As discussed before, the titanium ion is comprised by a band structure with electrons at “d” valence layer, whose necessary energy for band transition generates high optical absorption bands in the higher temperature radiation spectral region. For this reason, an emissivity measurement at higher temperature (1500°C) was conducted and the results are presented in Figures 3.

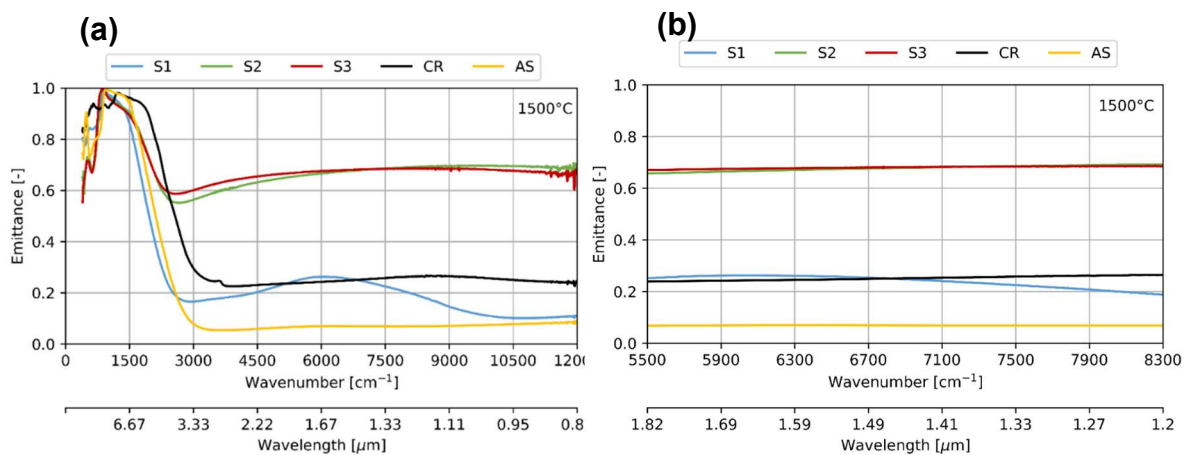


Figure 3 – Emissivity values at 1500°C as a function of the wavenumber and the wavelength for S1, S2, S3, CR and AS samples. (a) Full spectrum of thermal radiation and (b) neighborhood of the critical wavelength at 1500°C ( $\lambda_{c1500^\circ\text{C}} = 1.63 \mu\text{m}$ ).

The results at 1500°C makes it easy to realize that, although able to take different ions as a solid solution, the regular spinel structure itself (S1) is not a strong candidate for manufacturing high-emissivity coatings, as its emissivity does not even reach 0.3. The titanium-containing spinel compounds (S2 and S3), on the other hand, had their emittance values scaled up to double the value of S1. These improvements attested the optimization of the spinel structure absorption mechanisms, such as the electronic transition and lattice displacement, by adding a tetravalent ion into its interstices. Considering the positive influence of  $Ti^{4+}$  on the emissivity behavior of the studied materials, two other compositions containing a higher percentage of titanium in their structure were produced and evaluated. As it would be difficult to increase the presence of titanium in the spinel lattice, titanates were chosen instead.

For this part of the work, magnesium dititanate -  $MgTi_2O_5$  and zirconium titanate -  $ZrTiO_4$  (T1 and T2 samples) were selected as potential high emissivity compounds., Table II depicts the phase quantification of T1 and T2 samples calculated via the XRD technique, where the two phases were mostly present after the heat treatment for 7 hours at 1500°C. It is worth mentioning here that the amount of  $ZrTiO_4$  formed in T2 was not as high as the  $MgTi_2O_5$  in T1 due to the lower purity zirconium oxide used as the raw-material precursor, which led to the formation of several other secondary phases.

Table II – Phase quantification of titanate samples T1 and S2.

Phase identification	Phases quantity (%-wt.)	
	(T1)	(T2)
<b>MgTi<sub>2</sub>O<sub>4</sub></b>	97.0	-
<b>MgTiO<sub>3</sub></b>	3.0	2.6
<b>ZrTiO<sub>4</sub></b>	-	72.4
<b>TiO<sub>2</sub></b>	-	5.7
<b>SiO<sub>2</sub></b>	-	6.3
<b>Others</b>	-	13.0

The emissivity values attained for the titanate samples at 1000°C and 1500°C are presented in Figure 4 and Figure 5 and plotted again compared with the alumina-based substrate and the commercial coating reference in two different visualizations: as a function of the whole spectrum range or at the neighborhood of the critical wavelengths ( $\lambda_{c1000^\circ C} = 2.28 \mu m$  and  $\lambda_{c1500^\circ C} = 1.63 \mu m$ ).

Besides the comments already pointed in the previous discussion, one can notice that the pseudobrookite and the  $\alpha PbO_2$  structures of  $MgTi_2O_5$  and  $ZrTiO_4$ , respectively,



are not suitable for guaranteeing a high emissivity performance, as T1 and T2 showed emissivity values at 1000°C as low as the ones seen for the spinel samples ( $\epsilon < 0.4$ ). However, the presence of ions containing electrons at the “d” valence layer and its positive effect on the absorption mechanisms at high temperatures definitely seems to be a key aspect. The titanate samples T1 and T2 presented the highest emissivity values among all the samples evaluated here at 1500°C ( $\epsilon > 0.7$ ). Moreover, the joint presence of  $Zr^{4+}$  and  $Ti^{4+}$  in the same structure in T2 helped its emissivity to reach a considerable value of  $\epsilon = 0.85$ .

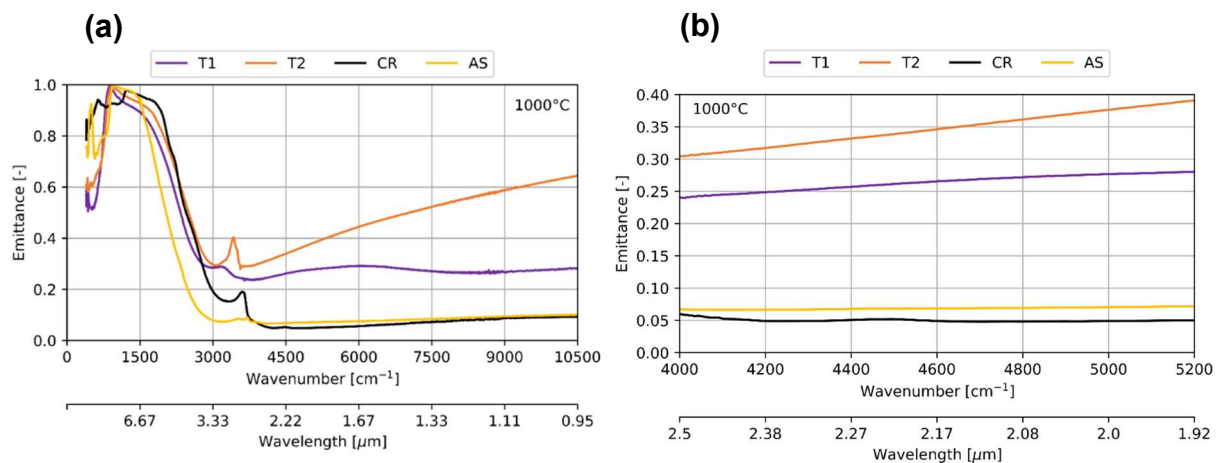


Figure 4 – Emissivity values at 1000°C as a function of the wavenumber and the wavelength for T1, T2, CR and AS samples. (a) Full spectrum of thermal radiation and (b) neighborhood of the critical wavelength at 1000°C ( $\lambda_{c1000^{\circ}C} = 2.28 \mu m$ ).

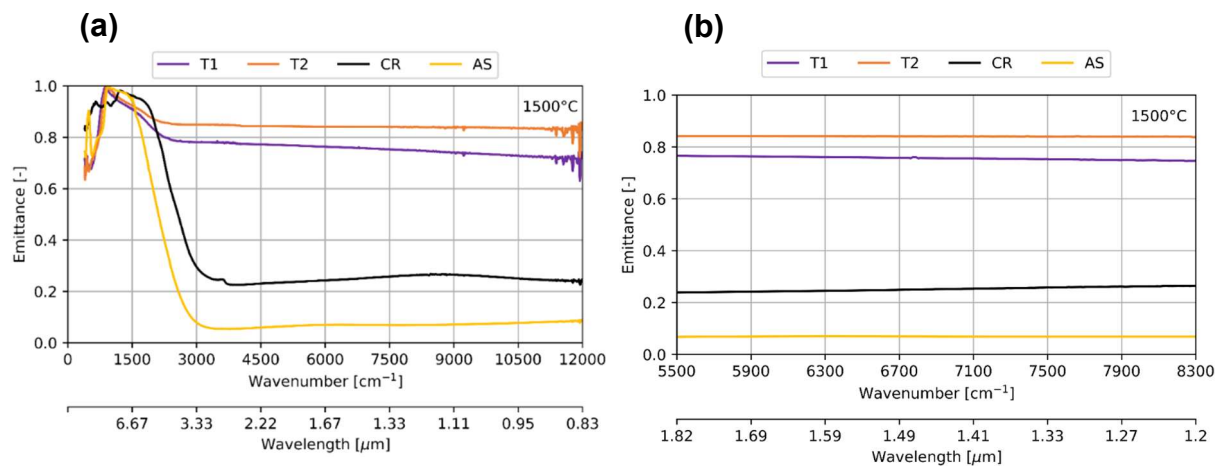


Figure 5 – Emissivity values at 1500°C as a function of the wavenumber and the wavelength for T1, T2, CR and AS samples. (a) Full spectrum of thermal radiation and (b) neighborhood of the critical wavelength at 1500°C ( $\lambda_{c1500^{\circ}C} = 1.63 \mu m$ ).

These results point out an important technological advance, such as the application of a coating containing any of the modified spinel or the titanate compounds on the surface of a high-alumina refractory wall would increase the thermal efficiency of a furnace operating at high temperatures. In addition, they would also provide a more consistent efficiency result than the reference commercial coating available on the market, which relies on emissivity values and do not match the operational conditions. Finally, the compositions developed in this work present costs which are relatively much lower than the ones of other high-emissivity components usually reported in the literature, such as the tantalum-based ceramics.

## **CONCLUSIONS**

By correctly understanding the mechanisms behind the interaction between photons and matter, optimized and engineered crystalline structures were proposed and successfully developed by adding a tetravalent large ion in order to maximize the radiation absorption. The results showed that the titanium-containing compositions, either in the spinel structure or as titanates, helped to reach significantly higher emissivity values, mainly at 1500°C, confirmed for the high emissivity result ( $\epsilon = 0.85$ ) attained by the combined use of titanium and zirconium.

When in operation, however, a ceramic coating is subject to installation-related issues, potential reactions with the processes and combustion gases as well as constant thermal cycles. Considering this aspect, further studies regarding the effect of the methodology of the application used, soot layers over the coating and its overall thermal cycle resistance may provide the necessary information for proposing a new generation of cost effective, theoretical based thermal coatings for high-temperature furnaces.

The current work additionally pointed out the importance of an assertive and careful characterization of the emissivity values, which is of the utmost importance when aiming at real energy savings in industrial applications. Due to the correct measurements and analyses, it was possible to validate the potential use of low-cost oxides in high-emissivity coating formulations.

## REFERENCES

1. W. H. Chen, Y. C. Chung, J. L. Liu. Analysis on energy consumption and performance of reheating furnaces in a hot strip mill. *International Communications in Heat and Mass Transfer*, 32 [5], (2005) 695-706.
2. M. Hasanuzzaman, R. Saidur, N. A. Rahim. Energy and economic analysis of an annealing furnace. *International Journal of Physical Sciences*, 6 [7] (2005) 1257-1266.
3. K.I. Iloff, M.F. Shafer, Space shuttle hypersonic aerodynamic and aerothermodynamic flight research and the comparison to ground test results, NASA Tech. Memo. 4499 (1993) 1–27.
4. G. Demetrius A. Kourtides, S.J. Rex A. Churchward, H. David M. Lowe, Protective Coating for Ceramic Materials, United States Patent 5296288 (1994) 1-13.
5. M. Švantner, P. Honnerová, Z. Veselý, The influence of furnace wall emissivity on steel charge heating, *Infrared Phys. Technol.* 74 (2016) 63–71. <https://doi.org/10.1016/j.infrared.2015.12.001>.
6. S. Hanzawa. Reduction of energy consumption during sintering through controlling of emissivity, *Journal of the Technical Association of Refractories*, 33 [4], 236-244 (2013).
7. G. J. Heynderickx and M. Nozawa. High-emissivity coatings o reactor tubes and furnace walls in steam cracking furnaces. *Chemical Engineering Science*, 59, 5657-5662 (2004).
8. J. Juthapakdeeprasert, O. G. Diaz, W. Lerdprom, D. De Sousa Meneses, D. D. Jayaseelan and W. E. Lee. Reactions and emissivity of cerium oxide with phosphate binder coating on basic refractory brick, *International Journal of Applied Ceramic Technology* 17 [2] (2020), 668-676.
9. Stewart D.A., Leiser D.B., DiFiore R.R., Katvala V.W. High efficiency tantalum-based ceramic composite structures. Vol. 1, United States Patent. 7767305, 2010. p. 1–16.
10. J. Zhang, B. Hao, X. Zhang, H. Yuan, Z. Zhang, L. Yang, The influence of microstructure and emissivity of NiO-Doped Fe<sub>3</sub>O<sub>4</sub>-spinel structure on near- and middle-infrared radiation, In: *Characterization of Minerals, Metals and Materials Conference Proceedings 2019*, Springer International Publisher, 69-77 (2019).
11. Gonzaga, F. B.: Development of an emission spectrometer for the near infrared region. PHD Thesis, Chemistry Department of Campinas State University, Campinas – SP. (2006) (In Portuguese).
12. Halenius, U.; Skogby, H.; Andreozzi, G. B.: Influence of cation distribution on the optical absorption spectra of Fe<sup>+3</sup> bearing spinel s.s.-heryncite crystals: evidence for

electron transitions in Fe<sup>+2</sup>-Fe<sup>+3</sup> clusters. *Physics and Chemistry of Minerals*. 29 (2002) 319-330.

13. Kingery, W. D.; Bowen, H. K.; Uhlmann, D. R.: *Introduction to Ceramics*. 2nd ed. John Wiley & Sons (1976) 646-703.

14. Zhang, S., Lee, W. E. Spinel-Containing Refractories, *Refractories Handbook*, 1<sup>st</sup> edition, Charles Schatt, p. 215-258 (2004) EUA.

15. Nakagomi, F.: Effects of cation distribution on structural properties of quaternary nanoparticles Zn<sub>x</sub>Mg<sub>1-x</sub>Fe<sub>2</sub>O<sub>4</sub> e Zn<sub>x</sub>Co<sub>1-x</sub>Fe<sub>2</sub>O<sub>4</sub>. PhD Thesis, Physics Institute of Brasília University, Brasília-DF. (2014) (In Portuguese)

16. De Sousa Meneses, D., Melin, P., Del Campo, L., Cosson, L., Echegut, P. Apparatus for measuring the emittance of materials from far infrared to visible wavelengths in extreme conditions of temperature, *Infrared Phys. Technol.* 69 (2015) 96–101. <https://doi.org/10.1016/j.infrared.2015.01.011>

17. Rousseau, B., Brun, J.F., De Sousa Meneses, D., Echegut, P. Temperature measurement: Christiansen wavelength and blackbody reference. *International Journal of Thermophysics*, 26 [4] (2005) 1277-1286. DOI: 10.1007/s10765-005-6726-4.