

Porous $\text{TiO}_2\text{-Y}_2\text{O}_3$ Ceramics with Specific Infrared-Optical Properties

G. Steinborn^{*1}, G. Tzschichholz¹, J. Guenster¹, M.H. Keller², J. Manara²

¹BAM Federal Institute for Materials Research and Testing, Unter den Eichen 87, 12200 Berlin (Germany);

²Bavarian Center for Applied Energy Research (ZAE Bayern), Am Hubland, 97074 Würzburg (Germany)

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Abstract

The infrared-optical properties and particularly the emissivity of sintered ceramics depend on the material's bulk properties and structural properties such as porosity, pore size distribution and pore diameter. The infrared-optical properties can be varied across a wide range by specifically selecting the material's bulk and structural properties. A major concern of the present study is the development of a ceramic coating material with a total emissivity below 0.2 at a temperature of 800 °C. For this purpose, various samples of a $\text{TiO}_2\text{-Y}_2\text{O}_3$ (TY) ceramic composite were produced with different properties. On variation in the Y_2O_3 content from 5 to 60 wt%, the porosity of the ceramic composites varies from 3 % to 47 % with the mean pore diameter lying in a range from 0.3 μm to 1.7 μm . The addition of graphitic pore builders increases the porosity up to 60 % and the mean pore diameter to a maximum of 15 μm . By optimizing the total porosity and the pore size of the TY ceramics, a total emissivity as low as 0.17 at 800 °C could be achieved.

Keywords: Oxide ceramic, porosity, mean pore diameter, infrared optical properties, emissivity

I. Introduction

Ceramic materials are used increasingly in industrial high-temperature range applications. Over 50 % of all industrial processes involve thermal steps. Consequently, it is clear that optimizing heat transport via a medium or between surfaces is both economically and ecologically relevant. In the aeronautical industry it is state of the art to coat the blades of gas turbines with ceramics that have low heat conductivity and high total emissivity. This high emissivity enables the thermal energy transmitted by forced convection to the ceramics to be efficiently radiated. On the other hand, there are applications where a low total emissivity is required. For example, in the automotive industry, coating hot parts such as exhaust manifolds, turbocharger housings or catalytic converters with a low-emissivity ceramic material could markedly reduce heat loss to the surrounding, temperature-sensitive components. Firstly, this leads to an increase in the engine's level of efficiency. Secondly, it permits temperature-sensitive, e.g. lightweight design materials to be used in the surroundings of the drive aggregate, which until now could not be used owing to the temperatures involved. Components made of metal also have a low emissivity. However, if they are used at high temperatures, oxidation processes occur, which cause the emissivity of the material's surfaces to rise considerably.

To obtain a comprehensive picture of heat transfer through a material, precise knowledge of all physical and chemical, macroscopic and microscopic properties is necessary. It is equally important to understand the relationships between these properties and their contribution

to heat conduction, thermal radiation and their coupling. Thus, for example, the complex refractive index for pure materials is published in the technical literature^{1,2}. However, even the presence of porosity below one percent or an impurity or material mixture can considerably impair the optical properties of the material, but exact knowledge of these influences enables targeted adjustment of infrared optical properties and thus accommodation of the scope of the material.

Besides their mechanical properties, both the thermal and the radiative properties of the ceramics play an essential role in such applications. Their particular application as a thermal barrier material is based on the reduction of the conductive heat transfer through the ceramic media as well as the radiative heat transfer. The infrared optical properties and thus the emissivity of the sintered ceramics depend on the material's bulk properties, such as refractive indices and electric conductivity as well as on their structure, which is mainly defined by the porosity and the pore size distribution³⁻⁵.

The emissivity ϵ of a material is a measure of its ability to emit radiative energy from its surface. The emissivity is defined as the ratio of energy radiated by a material's surface to the energy radiated by a black-body radiator at the same temperature. It is directly proportional to the total amount of energy, in W/m^2 , emitted via radiation from a surface at a given temperature. A black-body radiator is a theoretical object with an emissivity of 1 and thus emitting the maximum amount of energy via radiation at a given temperature. In the case of radiative properties, the spectral emissivity is also important. The spectral emissivity is the ratio of the radiation emitted by a surface at a specific wave-

* Corresponding author: gabriele.steinborn@bam.de

length to the radiation emitted by a black-body radiator at the same wavelength and temperature.

The objective of this study is the development of a ceramic material whose total emissivity is below 0.2 at 800 °C. The heat transfer of such ceramics owing to thermal radiation would be significantly lower than conventional ceramics (e.g. PYSZ coating), which have a total emissivity of up to 0.8 at the same temperature⁴. As mentioned before, a possible application is the automotive sector, where hot parts such as exhaust manifolds or catalytic converters can be coated with ceramic on the outer surface. The heat exchange with surrounding components would be significantly reduced. Similar applications in other sectors with the same or similar requirements are feasible. Altogether, the reduction of the emissivity offers a considerable potential for heat transfer optimization⁵.

Metallic assemblies used in the automotive field as part of the engine's exhaust system can reach temperatures up to 1000 °C. At these temperatures, heat emission occurs mainly through radiative emission in the infrared spectral range from the part's surface. Normally, clean metallic surfaces have a total emissivity of 0.1 or even lower. Metal components that are used at high temperatures are subject to oxidation processes. Generally this increases their total emissivity dramatically, to above 0.8. A reduction of the total emissivity from 0.8 to 0.2, e.g. with a ceramic coating, would lower the radiative heat transfer by about 70 %³. At room temperature, the contribution of radiation and free convection to the total heat transfer are in the same order of magnitude. In contrast, at a temperature of 800 °C, the heat transfer based on radiation is more than three times higher than the heat transfer by free convection⁴.

If suitable materials or material systems can be synthesized with a suitable structure so that they become predominantly impermeable to thermal radiation and only emit a small amount of it, it is possible to achieve a marked reduction in radiative heat transfer. Reducing the emissivity from the functional materials or material systems that are optimized for thermal radiation produces potential for energy efficiency and operating safety of temperature-loaded components.

II. Theory

Ceramics are mainly semi-transparent in the infrared-optical spectral range. This means that only a small part of the thermal radiation passes through the sample without being scattered or absorbed⁶. In porous media, the thermal radiative heat transfer through the medium will be significantly influenced by scattering and absorption processes. In general, scattering occurs at the interface of materials with different refractive indices and depends on the degree of difference in the refractive indices. In our case, scattering mainly takes place at the air-filled pores within the ceramic and at the interface between medium and environment, which is usually air. The absorption occurs in the ceramic material itself. As a high absorption coefficient also leads to a high level of emission, it is necessary to minimize absorption in the bulk material⁷. Together with maximization of the scattering effects in the relevant spectral range, the emissivity of a ceramic can be significantly reduced^{3,8}.

Particularly in semi-transparent media such as ceramics, radiative heat transfer together with heat conduction via the solid framework contributes significantly to the total heat transfer through the medium. In numerous porous materials with low densities, thermal radiation accounts for a proportion of up to 20 % even at room temperature⁹. Examples of this are thermal insulating materials such as mineral wool or polystyrene foam. With rising application temperature, the significance of thermal radiation compared to other heat transfer mechanisms increases dramatically. This is due to the strongly non-linear temperature dependence ($\sim \tau^3$) of the radiative heat transfer¹⁰.

As oxide ceramics are largely semi-transparent in the near infrared spectral range, their infrared-optical properties have a strong volume dependence. Scattering effects in particular influence the total emissivity of the ceramics. By manufacturing porous ceramics from pulverized starting materials in a sintering process, the scattering of electromagnetic waves is optimized in the ceramics. Here, an increase in scattering effects leads to a drop in the total emissivity. One option is the manufacture of porous composite ceramics. Composites consist of two-phase or multi-phase materials. If oxides with differing sintering behaviour are used, it is possible to manufacture porous ceramics under unchanged sintering conditions such as time and temperature. As a result, the pore diameters can also vary within a size range, in which radiation is scattered to an increased extent in the infrared spectral range.

The scattering of electromagnetic waves on spherical particles is described by the Mie theory¹¹. It shows that the scattered radiation is both dependent on the pore diameter and on the complex refractive index of the surrounding material. The air-filled pores in porous ceramics can thus be described approximately by an effective diameter even if they are not exactly spherical. Porosity and pore diameter can be influenced by the sintering conditions and the grain size of the starting powder as well as by special pore builders¹². These additives combust during the sintering process and leave behind pores of a defined size. As part of this study, in order to investigate this effect in more detail, composite ceramics are manufactured from metal oxide starting powders using different pore builders and then infrared-optically characterized.

The aim is to significantly reduce the total emissivity of composite materials at high temperatures in order to greatly reduce thermal radiation to the surroundings. For this purpose, composite materials based on oxide-ceramic nanopowders are manufactured and characterized structurally, by means of X-ray scattering and infrared-optical measurements. With the variation in manufacturing conditions, the ceramics can be altered in their structure. In order to achieve this goal, it is necessary to know the dependence of the emissivity firstly on the structure of the material and secondly on the complex refractive index of the material used. The complex refractive index is obtained from the microscopic properties such as the arrangement and symmetry of the atoms in the crystal lattice and the character of its chemical bond¹³.

In order to understand the emission of a porous body, precise knowledge of the complex refractive index

$m = n + ik$ of the material is required¹⁴. In the case of porous ceramic materials, a high real part n of the complex refractive index causes a high reflection at the air-medium interface and the air-filled pores within the ceramic. Additionally, a small imaginary part k results in a low absorption coefficient. To achieve a low emissivity, a high real part n and a small imaginary part k is required³. Therefore, the complex refractive indices of different ceramic materials were compared to draw up a shortlist of suitable starting materials which fulfil both conditions.

According to Wien's displacement law¹⁵ the radiative maximum of a black body is at a wavelength λ of about 2.7 μm for 800 °C. At this temperature, the majority of the radiative energy (~98 %) is emitted in the range between 0.25 μm and 18 μm . From a wavelength of approx. 5 μm and especially above 10 μm , multiphonon and single phonon processes contribute towards radiation absorption depending on the material. In order to minimize the contribution of these absorption mechanisms to the increase in emissivity, the material used should display the highest possible real part and the lowest possible imaginary part of the complex refractive index. As already mentioned, the complex refractive index is known for many pure materials. On the other hand, there is only a small amount of data available in the literature for mixtures of several substances, particularly for high temperature and higher wavelengths. For this reason, the complex refractive index was determined on non-porous composite ceramics.

For oxide ceramics, the spectral emissivity in the wavelength range between 1 μm and 5 μm is relatively low. At higher wavelengths, a strong increase can be observed. This behaviour can be recognized in Fig. 1, which shows the spectral emissivity of five different ceramic materials. The spectra were calculated from the measurement of the directional-hemispherical transmittance and reflectance at room temperature in the wavelength range from 0.25 to 18 μm . More than 30 % of its total radiation is emitted at wavelengths above 5 μm . Due to this fact, the spectral emissivity in this wavelength range still has a significant influence on the total energy emitted by radiation. To allow a simplified comparison of the emissivity of different materials, the total emissivity can be calculated from the spectral measurements with the Rosseland weighing function. The total emissivity is a temperature-dependent material constant proportional to the amount of energy which is emitted by a surface at the given temperature. In this paper, all values of the total emissivity are given for the desired application temperature of 800 °C.

Fig. 2a shows the real part n for some selected ceramics. Although all materials show a similar run with relative high n values at short wavelengths and a continuous decrease with increasing wavelength, some important differences can be identified. In particular, the TiO₂ shows a real part n higher than all other materials considered for wavelengths up to 7 μm . This is combined with a stronger decrease at smaller wavelengths than the other ceramics. On the other hand, the Al₂O₃ shows a small real part n across the entire observed spectral range which leads to less scattering and therefore to a higher total emis-

sivity. The imaginary parts k are presented in Fig. 2b. It is very apparent that BaTiO₃ has a relatively high k at short wavelengths, which leads to the expectation of a stronger absorbance at short wavelengths. Y₂O₃ shows a k that over the entire spectral range is one or two orders of magnitude lower than that of the other ceramics. For this reason, no strong absorption peaks can be observed in the emissivity spectrum.

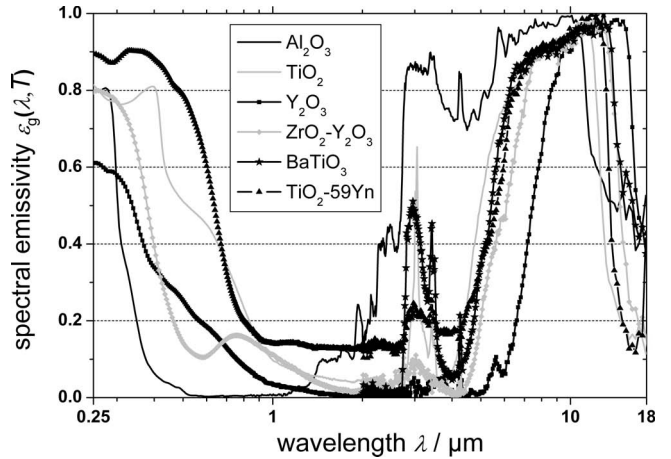


Fig. 1: Spectral emissivity of the ceramics Al₂O₃, TiO₂, Y₂O₃, ZrO₂-Y₂O₃, BaTiO₃ and the TiO₂-59YN composite at room temperature.

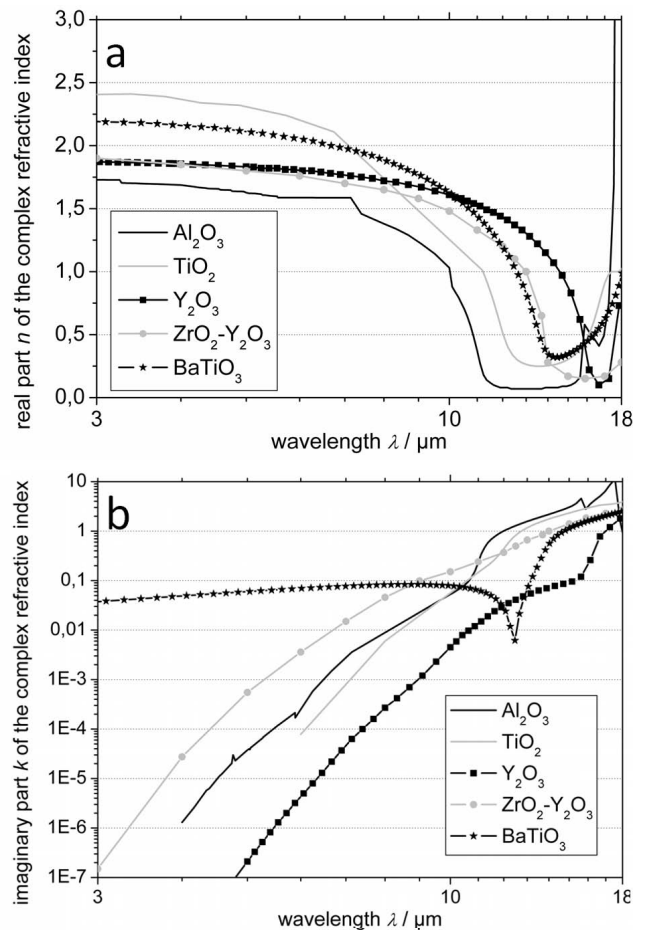


Fig. 2: Real part n (a) and imaginary part k (b) of the complex refractive index of the ceramics Al₂O₃, TiO₂, Y₂O₃, ZrO₂-Y₂O₃ and BaTiO₃¹.

III. Experimental

For the presented investigations, two nanopowders, i.e. TiO₂-P25 and Y₂O₃-N as well as a submicron powder Y₂O₃-P were selected. The relevant material properties of these powders are summarized in Table 1.

The detected pure density of the TiO₂ powder measured with a gas pycnometer (AccuPyc 1330, Micromeritics GmbH) using helium as testing gas in accordance with DIN 66137¹⁶ was 3.9 g/cm³, 4.8 g/cm³ for the Y₂O₃-N and 5.0 g/cm³ for the Y₂O₃-P powder. The specific surface determined was between 40 and 50 m²/g for the nanopowders and 3.6 m²/g for the μ-Y₂O₃ powder Y₂O₃-P. The average particle sizes of each are in the range of 10 to 160 nm and between 3 to 15 μm respectively, measured with an ultrasonic spectrometer (DT1200, Quantachrome, Germany). Images of the powders obtained by transmission electron microscopy (TEM) and scanning electron microscope (SEM) are presented in Fig. 3. The TiO₂ (titania) powder mainly consists of anatase and small fractions of rutile but only the cubic crystalline phase was detected in the Y₂O₃ (yttria) powders.

Different mixtures were prepared from the pure oxide powders, and further processed for one hour in an attritor mill (Netzsch GmbH, Selb, Germany) with ZrO₂ grinding balls and the addition of distilled water and 10 vol% Uniox (PEG – polyethylene glycol, molecular weight 20.000 g/mol, Nippon oils & fats, Japan) based on the respective solid content as pressing additive. Subsequently, the suspensions were dried in a freeze dryer to obtain compressible powders. The powders obtained were compacted at 100 MPa by means of uniaxial pressing to a green density from 45 to 48 % and sintered at different temperatures (1100–1600 °C, 10 K/min). Ceramics consisting of TiO₂-P25 with 5 to 60 wt% Y₂O₃-P and Y₂O₃-N were manufactured. Porosities and densities of the sintered samples were determined using the buoyancy-flotation method in accordance with DIN EN 993¹⁷. For samples with an open porosity greater than 10 %, the pore size distribution was analysed by means of mercury intrusion porosimetry^{18–20} according to ISO 15901²¹. The corresponding phases were identified by means of X-ray diffraction (Philips instrument PW 1710 copper anode, 40 kW, 25 mA, wavelength 0.154 nm Cu Kα). Furthermore, various pore-forming additives such as graphite (particle sizes between 2 and 8 μm) or carbon black (particle size below 50 nm) were added to selected samples.

For the preparation of graphitic additives containing samples, TiO₂-45Y₂O₃-P powders were dispersed in water and homogenized in an attritor mill (Netzsch GmbH, Selb, Germany) for one hour. After freeze-drying, the TiO₂-45Y₂O₃-P powders obtained were again dispersed in an aqueous suspension by means of conventional stirring with the addition of deflocculants CE64 (Zschimmer und Schwarz, Germany) or CTAB- Cetyltrimethylammonium Bromide (Fluka) and the pore builder graphite or carbon black (25 vol%). Freeze drying of this suspension results in a powder that was added (approx. 20 vol%) to a 10 wt% gelatin solution stirred for one hour at 40–50 °C. The suspension prepared in this way was poured into a mould and gelled at room temperature after approximately 30 min. Demoulding and freeze-drying for 24 hours provided samples ready for sintering. The burn-out temperatures of the graphitic powders, determined by differential thermal and thermal gravimetric analysis, were between 600 °C and 850 °C.

Polished sections from selected samples were prepared, thermally etched at 150 °C below the sintering temperature for approx. 15 min and their microstructure investigated by means of SEM. The spectral emissivity was determined by measuring the directional-hemispherical reflectance and transmittance of the ceramic samples with an integrating sphere at ambient temperature. A PerkinElmer Lambda 950 diffraction spectrometer was used for the wavelength range from 0.25 μm to 2.5 μm and a Bruker IFS 66v FTIR spectrometer was used for the wavelength range from 1.4 μm to 18 μm. The total emissivity at 800 °C was calculated according to the procedure described in the previous section.

IV. Results and Discussion

While retaining the same sintering conditions, the open porosity and the mean pore diameter of the sintered samples increased with increasing Y₂O₃ content in the TiO₂-P25 – Y₂O₃-P ceramic composite, see Fig. 4. Fig. 5 shows the total emissivity as a function of the Y₂O₃ content for the same set of samples. It is clearly noticeable that the emissivity monotonically decreased with increasing Y₂O₃ content. Simultaneously with increasing Y₂O₃ content, increasing phase content of yttrium titanate (Y₂Ti₂O₇) was observed, see Fig. 6. Therefore, at this point it is not clear whether the yttria-dependent decrease in the emissivity in Fig. 5 is a result of increasing porosity, pore diameter or yttrium titanate phase content.

Table 1: Key parameters of the investigated ceramic raw powders: manufacturer and manufacturing processes, particle size, specific surface area, true density and X-ray phase.

Powder	Manufacturing Process	Particle size /nm	S_m /m ² ·g ⁻¹	ρ_{rein} /g·cm ⁻³	X-ray phase
TiO ₂ -P25	Evonic Degussa AG, gas phase reaction	40–160	50	3.9	anatase, rutile
Y ₂ O ₃ -P	Projector GmbH, Precipitate	3,000–15,000	3.6	5.0	cubic
Y ₂ O ₃ -N	Chempur GmbH Precipitate	10–80	40	4.8	cubic

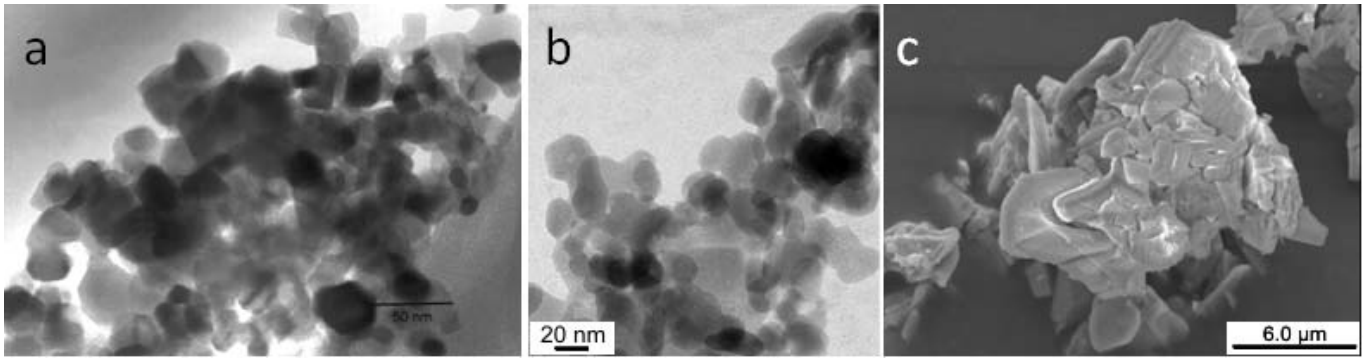


Fig. 3: TEM and SEM images of the ceramic raw powders: (a) TiO_2 -P25, (b) Y_2O_3 -N, (c) Y_2O_3 -P

Among the investigated ceramic composites, the T-45YP made of 55 wt% TiO_2 -P25 and 45 wt% Y_2O_3 -P shows the most promising results: a relative sintering density of 56 % and a total emissivity of 0.23. For higher yttria concentrations up to 60 wt%, similar results are obtained. Therefore, the T-45YP ceramic composite was investigated in more detail: T-45YP samples were prepared and sintered at temperatures between 1100 °C and 1600 °C. An increasing sintering temperature led to a decrease in the rutile content and to an increase in the yttrium titanate phase. The amount of yttrium titanate almost doubled as the sintering temperature increased from 1100 °C to 1600 °C. In contrast, the amount of yttrium titanate and rutile remained almost constant for the T-45YN system composed of 55 wt% TiO_2 -P25 and 45 wt% of the nanodispersed yttria powder Y_2O_3 -N. This is understandable in terms of the higher reactivity between the nanodispersed titania and yttria powders.

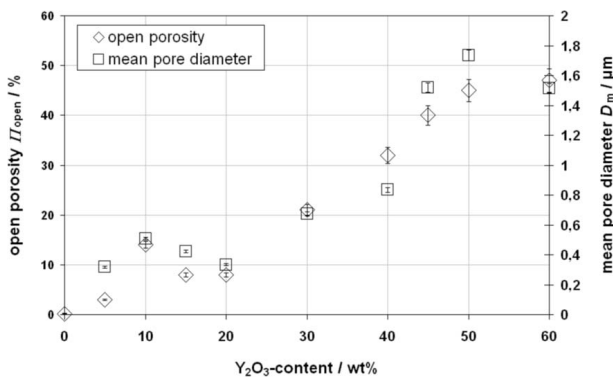


Fig. 4: Open porosity and mean pore diameter of the TiO_2 - Y_2O_3 ceramic system as a function of the Y_2O_3 content at a sintering temperature of 1300 °C.

The T-45YP system shows a total emissivity between 0.2 and 0.3 for the investigated sintering temperatures, in comparison to the T-45YN ceramics with a total emissivity ranging from 0.3 to 0.4. One reason for the higher emissivity of the T-45YN ceramic is the finer pore structure, as observed by means of SEM. The pores cannot interact effectively with the infrared radiation: They are too small to act as scattering objects for the radiation. This observation argues against the suggestion that merely the yttrium titanate phase concentration is responsible for the observed reduction in emissivity in Fig. 5. In turn, we can deduce

from the data that an increasing yttria content can reduce the emissivity of the sintered ceramic composites by forming a more porous structure with a pore size effective for infrared radiation scattering.

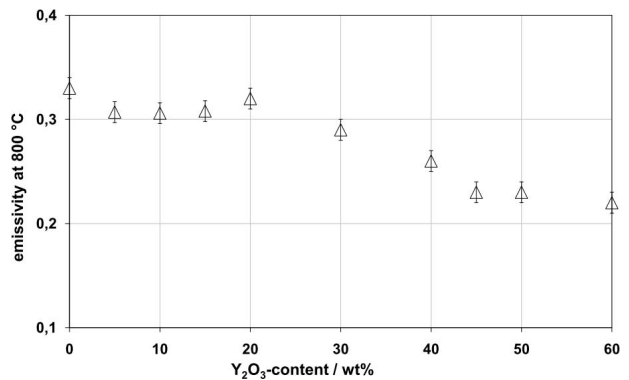


Fig. 5: Emissivity of the TiO_2 - Y_2O_3 composite at 800 °C sample temperature as a function of the Y_2O_3 content. The samples have been sintered at a temperature of 1300 °C.

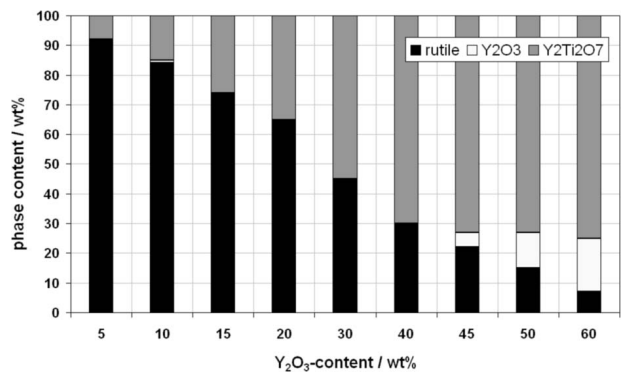


Fig. 6: Phase content in the TiO_2 - Y_2O_3 ceramic system as a function of Y_2O_3 content at a sintering temperature of 1300 °C.

According to this concept and in order to have more direct control over the samples' porosity and pore size, pore building additives were added to the samples. To achieve a very low total emissivity below 0.2, the mean pore diameter should be in the range of 2 to 6 μm , as shown in Fig. 7, together with a sufficiently high porosity of about 50 %. The use of pore building materials such as graphite and carbon black in the ceramic production process has a beneficial effect on the open porosity and the formation of pores larger than 2 μm . The corresponding data are summarized in Table 2.

Table 2: Detected characteristics of the ceramic systems T-45YP, made of 55 wt% TiO₂-P25 and 45 wt% Y₂O₃-P (μ -powder), and T-45YN, made of 55 wt% TiO₂-P25 and 45 wt% Y₂O₃-N (nano-powder), for different sintering temperatures and manufacturing processes. Standard preparation of the samples, e.g., T-45YP, was uniaxial pressing. Samples denoted by -Gel have been prepared by gel casting, +C stands for the addition of graphitic carbon (particle sizes between 2 and 8 μ m) and +CB stands for carbon black (particle size below 50 nm). Also, T_s is the sintering temperature, t_H time at max sintering temperature, ρ_{sinter} density after sintering, π_{open} open porosity of the samples after sintering, D_m mean pore diameter after sintering, $\varepsilon(800^\circ\text{C})$ total emissivity calculated at 800 °C sample temperature.

Ceramic system	T_s /°C	t_H /h	ρ_{sinter} /g·cm ⁻³	$\rho_{\text{sinter,rel}}$ /%	π_{open} /% [± 0.05]	D_m / μ m [± 0.02]	ε (800 °C) [± 0.01]
T-45YP	1100	2	2.4	51	49	0.53	0.32
T-45YP	1200	2	2.5	54	46	1.05	0.26
<i>T-45YP*</i>)	<i>1300</i>	<i>2</i>	<i>2.9</i>	<i>60</i>	<i>40</i>	<i>1.52</i>	<i>0.23</i>
T-45YP	1400	2	3.1	64	36	2.60	0.24
T-45YP	1500	2	3.9	82	18	2.55	0.26
T-45YP	1600	2	4.5	94	< 1	–	0.29
<i>T-45YP-Gel*</i>)	<i>1400</i>	<i>2</i>	<i>2.2</i>	<i>46</i>	<i>53</i>	<i>4.38</i>	<i>0.21</i>
<i>T-45YP+C-Gel*</i>)	<i>1400</i>	<i>2</i>	<i>2.1</i>	<i>43</i>	<i>56</i>	<i>4.70</i>	<i>0.18</i>
<i>T-45YP+CB-Gel*</i>)	<i>1400</i>	<i>2</i>	<i>1.7</i>	<i>36</i>	<i>61</i>	<i>5.67</i>	<i>0.17</i>
T-45YN	1100	2	2.8	58	42	0.31	0.40
T-45YN	1300	2	4.0	84	16	0.38	0.31
T-45YN	1400	2	4.7	97	< 1	–	0.29
T-45YN-Gel.	1400	2	2.1	44	45	15.7	0.27
<i>T-45YN+CB-Gel*</i>)	<i>1400</i>	<i>2</i>	<i>2.5</i>	<i>53</i>	<i>51</i>	<i>6.7</i>	<i>0.24</i>

*) Pores distribution unimodal

SEM images of two similar T-45YP samples with 25 vol% graphite as a pore building additive sintered at 1100 °C and 1400 °C, respectively, are shown in Fig. 8. The sample sintered at 1100 °C shows the formation of sintering necks and the coalescence of ceramic particles (intermediate stage of sintering). This sample with a porosity of 55 % and a pore size < 1 μ m has a total emissivity of 0.28. In contrast, the porosity of the ceramic sintered at 1400 °C is reduced to 42 % with a pore size > 2 μ m and a significantly reduced total emissivity of 0.20. However, it is not clear which exact total porosity is required for achieving the lowest emissivity. On the other hand, this example supports the viewpoint that it is not the total porosity of a sample that is the critical parameter for minimum emissivity, but the pore size.

Fig. 9 compares total emissivities of the T-45YP and T-45YN ceramics with and without pore building additives as a function of the sintering temperature for all investigated samples. The lowest emissivities were obtained in a sintering temperature range from 1300 °C to 1400 °C. With carbon black as pore building additive and a sintering temperature of 1400 °C, a unimodal pore size distribution between 2 and 6 μ m could be achieved. At lower

sintering temperatures the pores are too small to effectively interact with infrared radiation and at higher temperatures sintering results in a densification of the samples, reducing the total number of scattering centres, i.e. pores.

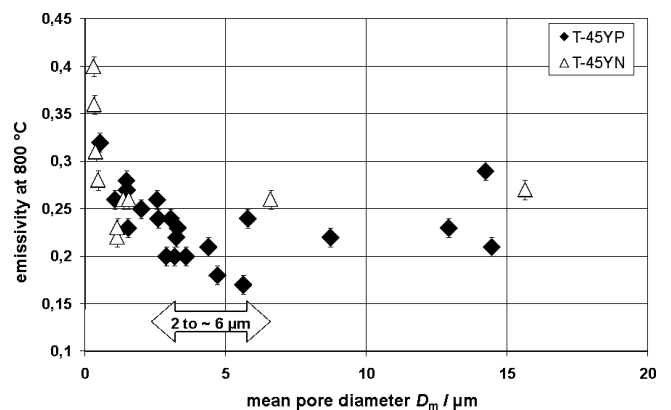


Fig. 7: Emissivity of the TiO₂-45Y₂O₃ ceramics (T-45YP, T-45YN) as a function of the mean pore diameter.

That could also be confirmed in the work of 22. The total emissivity rises considerably if the pores are too big (in a range from 50 – 200 μ m) ($\varepsilon_{\text{total}} = 0.66$ at 300 °C and 0.42 at 700 °C).

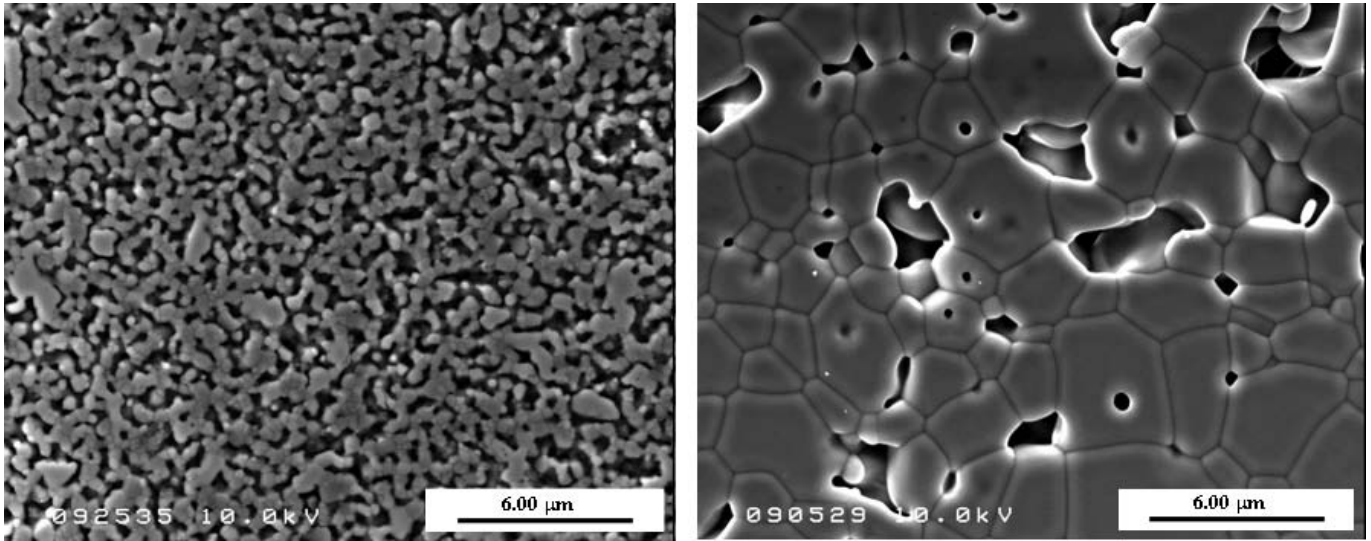


Fig. 8: SEM images of two T-45YP samples after sintering at two different temperatures, left, 1100 °C, right, 1400 °C (thermal etching condition 100 °C to 150 °C under sintering at temperatures for 15 min)

In contrast, the unimodal distribution of pores in the material provides a homogeneous grain structure and leads to homogeneous scattering behaviour in the IR spectral range, which is thus necessary for a low total emissivity. The results presented in Table 2 confirm this. When graphite (GJM-2) and soot were added to T-45YP, pore diameters of 4.4 μm and 5.7 μm could be measured with a total porosity of ~ 60 %, whereby the lowest total emissivities of 0.17/0.18 were obtained. The pore size distribution is unimodal and the pore size is very close to the wavelength ($\lambda \sim 3 \mu\text{m}$) where the black body shows its maximum intensity at 800 °C.

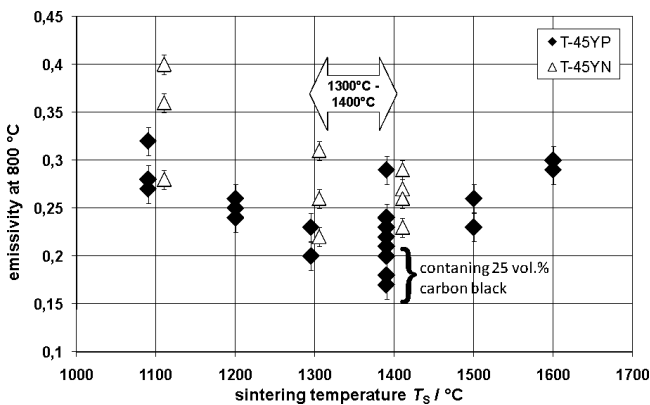


Fig. 9: Emissivity of the TiO_2 -45 Y_2O_3 ceramic (T-45YP, T-45YN), with and without pore builder, as a function of the sintering temperature.

Similar investigations²³ were performed on open-pored layer structures composed of titanium oxide and yttrium oxide (mass ratio $TiO_2:Y_2O_3 = 45:55$). The porosity of the layers sintered at 900 °C to 1200 °C is 40–50 %. With increasing sintering temperature, sintering proceeds (grain coarsening) and an increasing mean pore size was observed. The total emissivity at 800 °C is discussed for the sintering temperatures 1100 °C and 1200 °C. With higher sintering temperature, the total emissivity is lower (~0.3) than at 1100 °C (~0.4), which is due to the higher sintering

level and the pore size. According to ²³, the influence of pore structure and grain size of the crystallite on the total emissivity is considered to be great.

Sintering curves of the pure TiO_2 , T-45YP and T-45YP samples containing 25 vol% carbon black are presented in Fig. 10. It is clearly noticeable that densification of the T-45YP sample is significantly delayed relative to the pure TiO_2 sample. This effect is even more pronounced for the T-45YP sample containing carbon black.

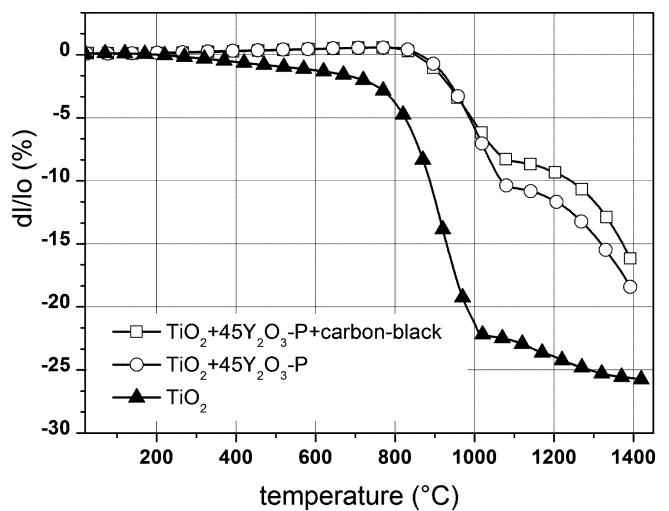


Fig. 10: Dilatometer analysis of sintering behaviour of the pure TiO_2 , T-45YP and T-YP with 25 vol% carbon black samples..

V. Conclusion

For the TiO_2 - Y_2O_3 (TY) ceramic composite, various samples were produced with different properties. With variation of the Y_2O_3 content from 5 to 60 wt% in the TY system, the porosity changes from 3 % to 47 % and the mean pore diameter lies between 0.3 μm and 1.7 μm.

The addition of the pore builders graphite and carbon black to the TY-ceramic increased the porosity up to 60 % and the mean pore diameter to a maximum of 15 μm. The porous materials have crystallite sizes ranging from 0.2 μm

to 4.6 μm . The total emissivity at 800 °C of the ceramic samples investigated was between 0.17 and 0.4.

Lowest total emissivities (below 0.2) of the $\text{TiO}_2\text{-Y}_2\text{O}_3$ ceramic composites are found at sintering temperatures between 1300 °C and 1400 °C, at which a porosity between 40 % and 60 % and a mean pore diameter between 2 and 6 μm could be reached.

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References

- Palik, E.D.: Handbook of optical constants of solids. Academic Press, San Diego, (1998).
- Garcia, G., Figueras, A., Merino, R.I., Orera, V.M., Llibre, J.: Structural and Optical Properties of Yttria-Stabilized-Zirconia Films Grown by MOCVD, *Thin Solid Films*, **370**, 173–178, (2000).
- Manara, J., Reidinger, M., Korder, S., Arduini-Schuster, M., Fricke, J.: Development and Characterization of Low-Emitting Ceramics, *Int. J. Thermophys.*, **28**, 1628–1645, (2007).
- Manara, J.: Infrared-optical radiative transfer for analysis of the structure and thermal conductivity of ceramics for high-temperature applications (in German), PhD dissertation at the Bavarian Julius-Maximilian-University of Wuerzburg, (2001).
- Keller, M.H., Manara, J., Tzschichholz, G., Steinborn, G.: Porous Ceramics with Optimized Infrared-Optical Properties, Proceedings 5th European Thermal-Sciences Conference, Editors: G.G.M. Stoffels, T.H. van der Meer and A.A. van Steenhoven, ISBN 978–90–386–1274–4, Eindhoven, (2008).
- Manara, J., Caps, R., Raether, F., Fricke, J.: Characterization of the Pore Structure of Alumina Ceramics by Diffuse Radiation Propagation in the Near Infrared, *Opt. Commun.*, **168**, 237–250, (1999).
- Manara, J., Caps, R., Fricke, J.: Characterisation of the Pore Structure of Ceramics via Propagation of Light and Infrared Radiation, *Int. J. Thermophys.*, **26**, 531–542, (2005).
- Rozenbaum, O., De Sousa Meneses, D., Echegut, P.: Texture and Porosity Effects on the Thermal Radiative Behavior of Alumina Ceramics, *Int. J. Thermophys.*, **30**, 580–590, (2009).
- Fricke, J., Caps, R., Hümmer, E., Döll, G., Arduini, M.C., DePonte, F.: Optically Thin
- Fibrous Insulations. Insulations Materials: Testing and Application, ASTM STP 1030, 575–586, (1990).
- Wagner, W.: Heat Transfer: Fundamentals (in German), Vogel Verlag, Würzburg, (1993).
- Mie, G.: Studies of the Optics of Turbid Media, Particularly Colloidal Metal Solutions (in German), *Ann. Physik*, **25**, 377–445, (1908).
- Mattern, A.: Interpenetrating Metal-Ceramic Composites with Isotropic and Anisotropic Al_2O_3 Reinforcement (in German). Department of Mechanical Engineering, University of Karlsruhe (TH), Dissertation, (2005).
- Kittel, C.: Introduction to Solid-State Physics (in German), 14th Edition, Oldenbourg Wissenschaftsverlag GmbH, Munich, (2005).
- Bohren, C.F., Huffmann, D.R.: Absorption and Scattering of Light by Small Particles, New York: John Wiley & Sons, (1983).
- Siegel, R., Howell, J.R.: Thermal Radiation – Heat Transfer. Washington: McGraw-Hill, (1981).
- DIN 66137–2:2004. Determination of Solid State Density – Part 2: Gas Pycnometry.
- DIN EN 993–1:1995. Methods of Test for Dense Shaped Refractory Products – Part 1: Determination of Bulk Density, Apparent Porosity and True Porosity.
- Giesche, H.: Mercury Porosimetry – a General Practical Overview, *Part. Part. Syst. Charact.*, **23**, 9–19, (2006).
- Hoffmann, D., Rübner, K.: Characterization of Mineral Building Materials by Mercury Porosimetry, *Part. Part. Syst. Charact.*, **23**, 20–28, (2006).
- Carruthers, J.D.: The Physical Significance of Mercury Porosity Hysteresis in the Characterization of Calcined Precipitated Alumina, *Part. Part. Syst. Charact.*, **23**, 61–71, (2006).
- ISO 15901–1:2005. Pore Size Distribution and Porosity of Solid Materials by Mercury Porosimetry and Gas Adsorption – Part 1: Mercury Porosimetry.
- Jackson, J.D., An, P., Fabregat, S.D.: Measurement of the Total and Spectral Emittance of a Microporous Ceramic Material, *High Temperatures – High Pressures*, **30**, [59], 523–529, (1998).
- Knote, A., Krüger, H.G., Kern, H., Manara, J.: Electrophoretic Coating for the Realization of Low-Emitting Ceramic Layers (in German), Thüringer Werkstofftag 2004, Schriftenreihe Werkstoffwissenschaften Band 18, Verlag Dr. Köster, Berlin, 97–102, (2004).