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Spectral and Total Emissivity of High-Temperature Materials[1]

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A number of various high emissivity coatings has been investigated in detail. Oxide ceramic coatings for rotating x-ray anodes must have a total emissivity greater than 0.8 in order to ensure efficient cooling in vacuum. Only one of the investigated coatings showed sufficient long-term stability. For thermal protection of reusable space transportation systems during atmospheric reentry, in addition to high emissivity, oxidation resistance is required. SiC coatings and special polysilazane-based coatings have been tested. Results of emissivity measurements before and after flight experiments on the Russian FOTON capsule are also available. In order to improve the reliability of (high-temperature) emissivity measurements Pt–Rh alloys, SiC, Al_2O_3 doped with Cr_2O_3, and graphite have been tested to assess applicability as reference materials for comparative emissivity measurements by various facilities.

KEY WORDS: coatings; C/C–SiC composites; emissivity; oxidation protection; polysilazane; reference materials; SiC coatings.

1. INTRODUCTION

The knowledge of total emissivity at high temperatures is important because the contribution of heat transport by radiation increases with rising temperature. Thermal control may demand highly emitting surfaces to improve heat dissipation and therewith to keep the maximum temperature below critical values. Typical examples of such applications are x-ray tubes with rotating anodes [1, 2] which are heated by an electron beam in vacuum up to temperatures of around 1600 K. Cooling in this case is essentially by

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radiation and special coatings had to be developed offering a high emissivity and good chemical stability during thermal cycling. Changes in the chemical composition may lead to variation in the emissivity, especially for oxide-based ceramic coatings, which are more or less transparent and, therefore, volume radiators with an essential contribution by scattering at the grain boundaries [3, 4]. This explains that slight variation of inclusion concentration may drastically change the radiation properties.

For the application in reusable space transportation systems, highly emitting materials must be used to protect critical components against overheating during atmospheric reentry [5]. Carbon-based materials—especially C/SiC composites—are generally acknowledged to be most appropriate for such applications. However, carbon-based materials must be protected against oxidation. This can be achieved by coating with oxidation resistant materials. Also, because of extremely high loading of the material during the reentry phase, chemical reactions at the surface, leading to variations of the emissivity, have to be taken into consideration.

The knowledge of the spectral emissivity is equally important, not only to measure radiation temperatures of such materials, but also to understand better the reason for an observed variation of total emissivity. Often the variation of the spectral emissivity with wavelength is much more influenced by a chemical reaction than the absolute value of the total emissivity, e.g., oxide formation at the surface may lead to a clear reduction of the emissivity in the visible and near-infrared regions.

Emissivity measurements at high temperatures are difficult, especially because of problems of accurately measuring the surface temperature. Of great benefit would be a comparison of emissivity measurements performed at several laboratories. This, however, calls for reference materials which are stable and reproducible with regard to the surface properties and related emissivity. In view of this potential application, the aim of the experimental program has been extended to select candidate reference material samples.

2. MEASUREMENT TECHNIQUE

The emissivity is measured, as described earlier [6, 7], by means of the radiation comparison technique. As Fig. 1 shows, the sample (15 mm in diameter, 3 to 6 mm thick) is heated by an electron beam in vacuum of 4×10^{-2} Pa. The temperature is measured in a radial hole of 1.2 mm diameter and 7 mm depth. A thermoelectric microsensor [8] is used to measure the total emissivity and the spectral emissivity by using band pass filters in the range 1.3. to 8.3 μm. For wavelengths between 0.5 and 0.95 μm a Linearpyrometer LP2 [9] is used, as well as for temperature

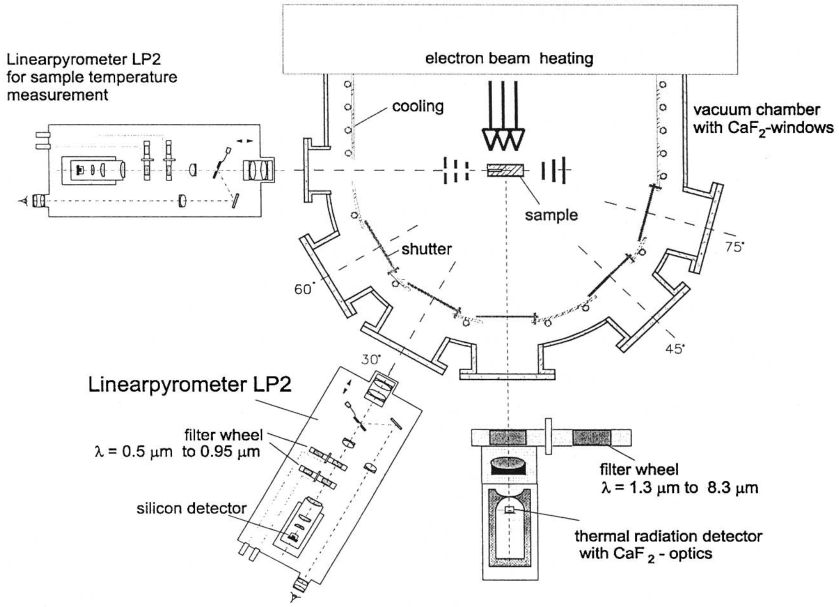

Fig. 1. Total and spectral emissivity measurement device.

measurement. The measurement accuracy is influenced mainly by the accuracy of the temperature measurement and extrapolation from the hole to the surface. The inaccuracy of the total emissivity and spectral emissivity above 2 μm is between 3 and 6% and, at shorter wavelengths, between 5 and 10%.

3. MEASUREMENT RESULTS

3.1. Coatings for X-Ray Anodes

Three different coatings have been investigated: the standard coating OT13 and two new so-called "Meltcoatings," ATZ and STZ. All coatings are oxide ceramics of different chemical composition as shown in Table I. The coatings were produced at Plansee, Reutte, Austria, and a detailed description of their structure is given in Ref. 10.

The samples were aged by annealing for 1 or 10 h in high vacuum (1×10^{-3} Pa) and at 1600°C. Figure 2 shows the total emissivity of the three coatings with two aging procedures. The highest emissivity could be achieved with OT13; however, after 10 h of aging, the values were much lower. Neither the values before nor those after aging are typical for

Table I. Chemical Composition of the X-Ray Anode Coatings [10]

Material	SiO_2 (wt%)	Al_2O_3 (wt%)	TiO_2 (wt%)	ZrO_2 (wt%)	CaO (wt%)
OT 13	–	87	13	–	–
ATZ	–	1–30	1–30	60–90	5–10
STZ	1–30	–	1–30	60–90	5–10

oxide ceramics, which usually decrease with increasing temperature in the range 0.3 to 0.6 μm. The high values are achieved by a special treatment of the coatings. The best stability is exhibited by the STZ coating, which therefore is favored because it assures high emissivity during the expected lifetime of the x-ray anode.

Thermal cycling tests during emissivity measurements between 800 and 1300 °C also demonstrated the stability of the STZ layer with respect to the emissivity. In Fig. 3 the time-dependent emissivity is plotted versus time measured at 1300 °C during 10 cycles.

3.2. Oxidation Protection Coatings for Reusable Space Transport Systems

C/SiC composites are generally established as the most appropriate materials to protect space transport systems during atmospheric reentry.

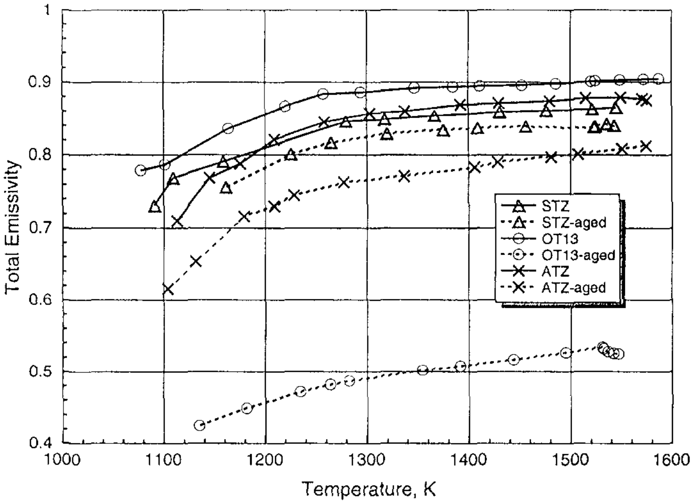

Fig. 2. Total normal emissivity of various x-ray anode coatings, measured after 1 and 10 h of annealing at 1600 °C.

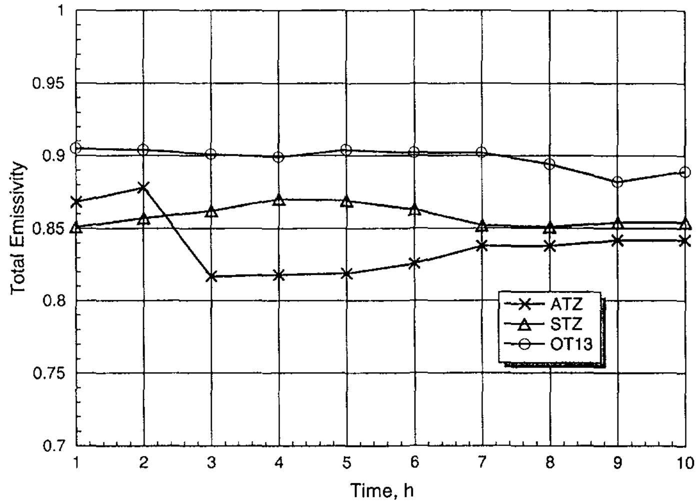

Fig. 3. Total normal emissivity of various x-ray anode coatings measured at 1300 °C during thermal cycling tests.

Results of the uncoated material produced by the German Aerospace Centre, DLR, Stuttgart, have been published earlier [11]. For practical application the surfaces have to be protected against oxidation. The emissivity behavior of the following two types of coatings has been investigated:

(a) SiC layers, produced by Schunk-Kohlenstofftechnik, Gießen, by multilayer CVD coating.

(b) Polymer-derived ceramic coatings, produced by dip-coating at Max Planck Institute for Powder Metallurgy, Stuttgart. Various coatings have been investigated in detail [12] with respect to mechanical and thermal stability. The base was a commercially available polysilazane Si–C–N (NCP 200; Chisso Corp.) and a modified boron-containing polysilazane (Si–B–C–N) [13]. The C/SiC samples were immersed in a solution of the corresponding polysilazane with toluene into which Si or SiC in the form of powder with particle diameters of 3.6 μm (Si) or 0.4 μm (SiC) and a volume content of 42% was mixed. Thereafter, the samples were subjected to a special thermal treatment procedure [12]. The following coatings have been used for emissivity measurements: (Si–C–N) + Si, (Si–C–N) + SiC, (Si–B–C–N) + Si, and (Si–B–C–N) + SiC.

The results of the total normal emissivity measurements are shown in Fig. 4. The maximum values have been achieved with SiC coating. Dip-coated samples show lower total emissivities, whereby adding Si leads to higher values, especially in the case of (Si–C–N). As Fig. 5 shows the difference between (Si–B–C–N) + Si and (Si–B–C–N) + SiC is negligible. The wavelength dependency of the spectral emissivity clarifies the differences. The (Si–C–N) + SiC coating (Fig. 6) shows increasing values starting at 0.5 μm indicating that SiO_2 was formed at the surface, whereas the spectral emissivity of (Si–C–N) + Si is more or less constant in the range 0.85 μm. In Fig. 7, the spectral emissivity of (Si–B–C–N) + Si is plotted, which is practically identical to that of (Si–B–C–N) + SiC (not presented) and the curves of (Si–C–N) + Si in Fig. 6.

Taking into account the radiation properties and the thermal and mechanical as well as the oxidation behavior, the polyborosilazane (Si–B–C–N) with Si seems to be the optimum coating. Reentry simulation tests with dip-coated samples are not yet completed. Reentry tests with SiC coatings are described in the next section.

3.3. Emissivity Measurements Before and After Atmospheric Reentry Tests

Thermal protecting materials of reusable space transport systems are exposed to very high heat fluxes, ranging up to 1.8 MW · m^{-2}. The

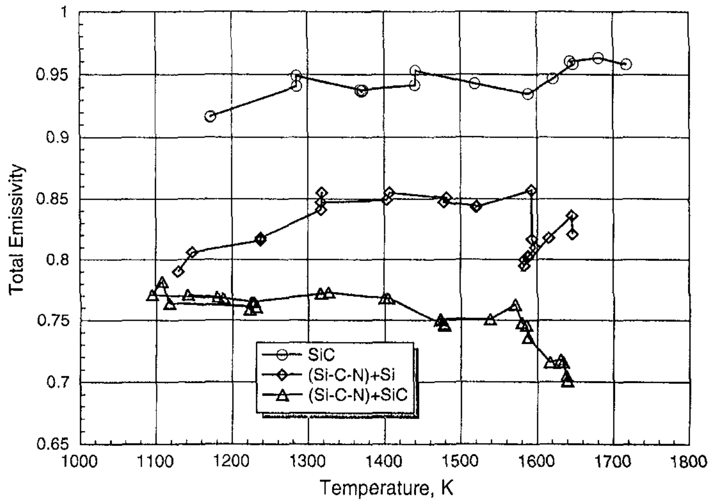

Fig. 4. Total normal emissivity of SiC and polysilazane coatings on C/C–SiC composites.

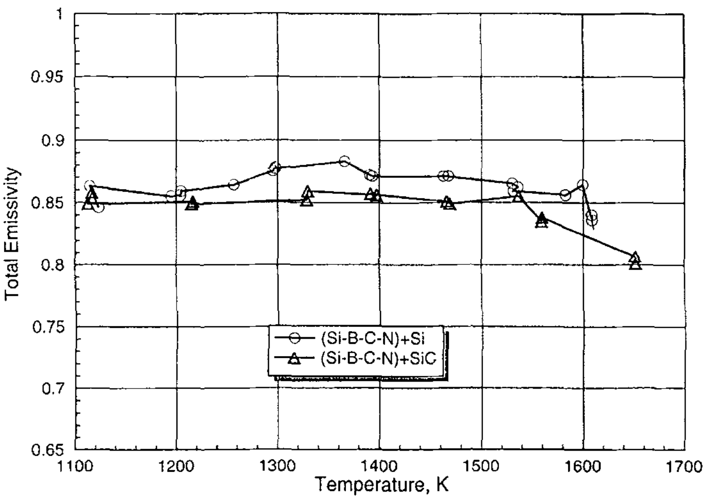

Fig. 5. Total normal emissivity of polyborosilazane coatings on C/C SiC composites.

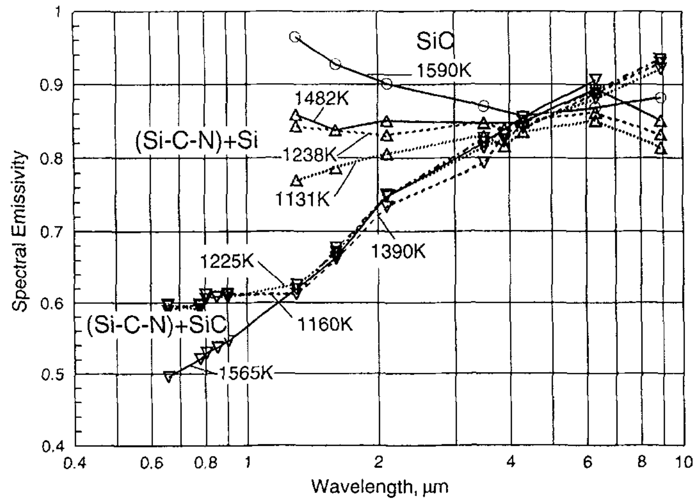

Fig. 6. Spectral emissivity of SiC and polysilazane coatings.

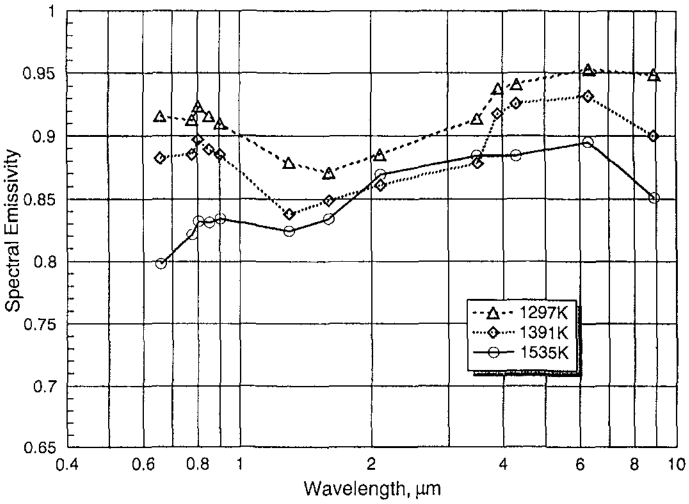

Fig. 7. Spectral emissivity of polyborosilazane coating at various temperatures.

maximum temperatures reached during the reentry are of the order of 2000 to 2100 °C. Material specimens of C/C–SiC composites, produced at DLR, Stuttgart, using the liquid silicon infiltration process (LSI), were tested on Russian FOTON capsule reentry flight experiments in 1992 and 1994 [14]. Two types of specimens were used:

(a) uncoated C/C–SiC and

(b) C/C–SiC coated with SiC by multilayer CVD coating with a total thickness of 98 μm.

The reasons for the coating were twofold: protection of the material against oxidation and increase of the emissivity. Figures 8 and 9 show the total and spectral emissivity results. The decrease in the spectral emissivity with wavelength of the uncoated, virgin material has been explained earlier in Ref. 15 by the contribution of the surface structure of the carbon fibers (T800). This behavior of the spectral emissivity and Wien's displacement law are the reason for the increase in the total emissivity with increasing temperature. The emissivity of the coated surface is nearly ideally close to 1.0. After the flight experiments two specimens were available to measure the emissivity again:

(a) FOTON F3 - CVD–SiC coated, after one mission; and

(b) FOTON F6 - uncoated C/C–SiC, after two missions.

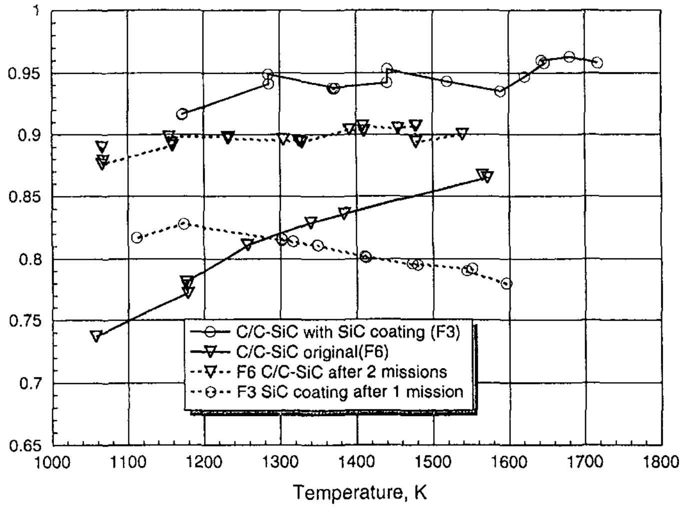

Fig. 8. The total emissivity of liquid siliconized C/C–SiC, uncoated and coated with SiC (multilayer CVD), before and after reentry tests.

The CVD coating completely disappeared at sample F3, and the total emissivity was much lower than that of sample F6, which increased in comparison with the virgin state of the material. At first glance this seems to be difficult to understand. However, spectral emissivity measurements in

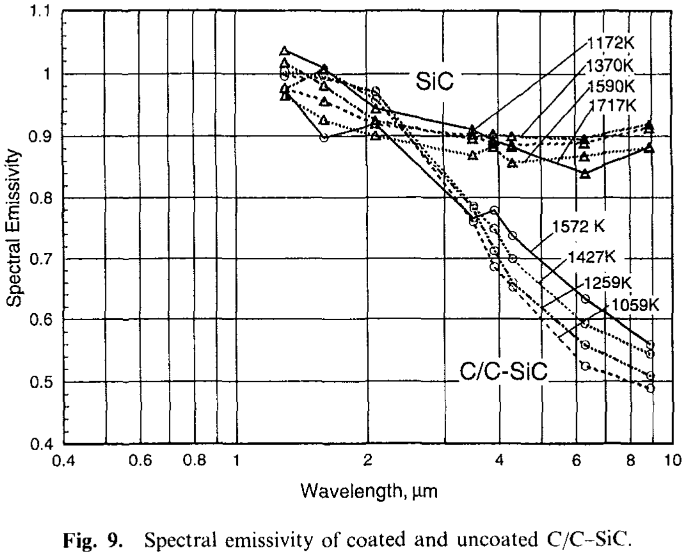

Fig. 9. Spectral emissivity of coated and uncoated C/C–SiC.

combination with surface mapping by means of energy-dispersive x-ray analysis (EDX) provide an explanation.

The hypothesis of the principal damaging process is given in Ref. 14 as follows:

(a) "active oxidation" during the first phase of reentry at a low pressure and high temperature leads to the reaction $SiC + O_2 \rightarrow SiO + CO$; and

(b) "passive oxidation" during increasing pressure and decreasing temperature leads to the formation of a thin self-protecting glassy surface layer by dissociation/reaction of SiC with air oxygen ($2SiC + 3O_2 \rightarrow 2SiO_2 + 2CO_2$).

If we compare the EDX pictures of the F3 and F6 specimens we find that the distribution of SiO_2, SiC, and C on the surface of sample F6 is nearly equivalent, whereas F3 clearly shows a predominance of SiO_2 and SiC. The dominance of SiO_2 explains the wavelength dependency of the spectral emissivity of sample F3 (Fig. 10), which is typical for oxide ceramics. The higher carbon content of F6 (protected by partly transparent glass layer) leads to increased emissivity values. Similar effects have been observed after thermal etching of C/C-SiC samples [15], leading to a disturbance of the fiber structure with low emissivity in the infrared. The total emissivity thereby increased in a similar amount as F6 after the second mission. In

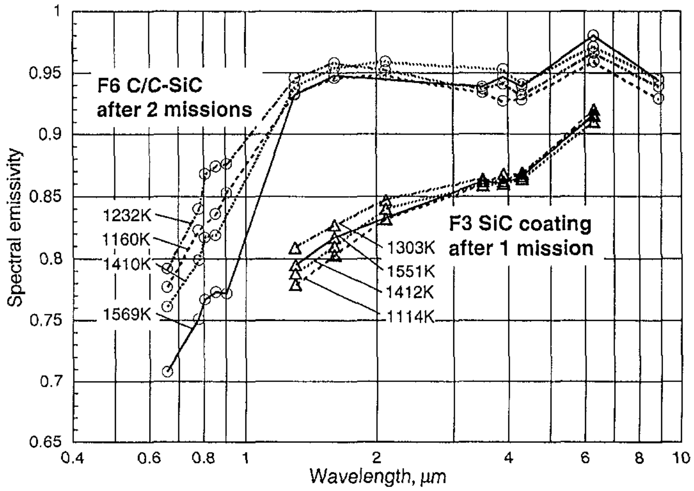

Fig. 10. Spectral emissivity of coated (F3) and uncoated (F6) C/C-SiC after reentry tests.

the visible range the spectral emissivity of F6 is lower (Fig. 10) and similar to the values of F3, explaining the similar visual appearance of both materials. The decrease in the total emissivity of F3 corresponds to the variation of spectral emissivity with wavelength and Wien's displacement law.

4. CONCLUSIONS

The results of the emissivity measurements demonstrated that a broad variation of the level of the total emissivity and, especially, of the wavelength dependency of the spectral emissivity can be expected, depending upon the material preparation, the thermal treatment, and the chemical reactions on the surface. Predictions are thereby very difficult, especially if oxidation takes place, leading to a reduction of the emissivity in the visible and near-infrared, in contrast to metal surfaces of which the emissivity increases by oxidation. As known from the literature, even low impurity contents in a pure oxide ceramic may lead to a drastic variation in the spectral distribution of the emissivity in the near-infrared range. In the case of the materials described in this paper, where the oxide layers are thin, the semitransparency of oxide further complicates the situation.

Referring to the uncertainties involved with high-temperature measurements, it would be useful to compare measurements carried out at

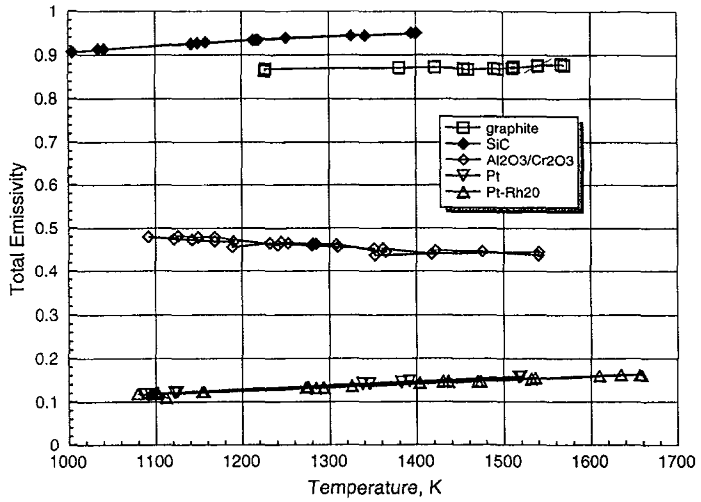

Fig. 11. Total normal emissivity of various materials selected as candidates for reference materials for emissivity measurements.

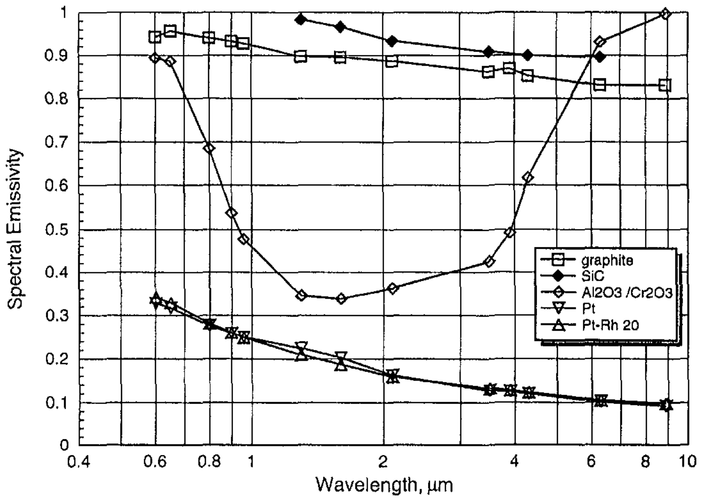

Fig. 12. Spectral emissivity of various materials selected as candidates for reference materials for emissivity measurements.

several laboratories. For that purpose, specimens are needed which are stable with regard to their emissivity and which can be prepared with a reproducible surface. During our measurements we tried to select a number of candidate materials which shall be included in a planned round-robin program by a couple of laboratories. In the high emissivity range, SiC (bulk material or coating) and graphite (isotropic, special surface treatment) have been stated [7] to be well suited. For low emissivity values, Pt–Rh alloys have been found to be useful because there is no danger of oxidation. The rodium content was varied between 0 and 40 vol% without a significant change in the emissivity.

Al_2O_3 doped with Cr_2O_3 seems to be appropriate to represent an oxide ceramic covering a broad range of spectral emissivity depending on, wavelength and with a total emissivity in the medium range. The results of our preliminary measurements are presented in Figs. 11 and 12.

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