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

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**ABSTRACT**

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 efficiently enough cooling in vacuum. Only one of the investigated layers showed a satisfying long term stability. For thermal protection of re-usable space transportation systems during atmospheric reentry, in addition to high emissivity, oxidation resistivity is required. SiC-coatings and special polysilazane based coatings have been tested. Results of emissivity measurements before and after flight experiments will the Russian FOTON capsule are also available. In order to improve the reliability of emissivity measurements Pt-Rh-alloys, SiC, $Al_2O_3$ doped with $Cr_2O_3$, and graphite have been tested with regard to the applicability as reference materials for intercomparative emissivity measurements.

KEY WORDS: C/C-SiC composites, emissivity measurements, emissivity reference materials, high emissivity coatings, oxidation protection layers, polysilazane, SiC-coatings, x-ray anode 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 radiation and special coatings had to be developed offering high emissivity and good chemical stability during thermal cycling. Changes of the chemical composition may lead to a variation of the emissivity especially at 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 little variation of inclusions may drastically change the radiation properties.

For the application at re-usable 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, what can be achieved by coating with oxidation resistant materials. Also here, because of extremely high loading of the material during the reentry phase, chemical reactions at the surface have to be taken into consideration leading to variations of the emissivity.

The knowledge of the spectral emissivity is equally important, but not only to measure radiation temperatures of such materials but also to better understand 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 region.

Emissivity measurements at high temperatures are difficult especially because of problems of accurately measuring the surface temperature. Of great importance would be an intercomparison of emissivity measurements carried out at several different 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 diameter, 3 to 6 mm thick) is heated by an electron

beam in vacuum of $4\times10^{-4}$ mbar. 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 mm to 8,3 mm. For wavelength between 0,5 mm and 0,95 mm a Linearpyrometer LP2 [9] is used as well as for temperature measurement. The measurement accuracy is mainly influenced by the accuracy of temperature measurement and extrapolation from the hole to the surface. The inaccuracy of the total emissivity and spectral emissivity above 2 mm 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 Tab.I. The coatings were produced at Plansee, Reutte, Austria and a detailed description of their structure is given in [10].

The samples were aged by annealing for 1 h or 10 h respectively in high vacuum ($1\cdot10^{-5}$ mbar) at 1600°C. Fig. 2 shows the total emissivity of the three coatings with two different aging procedures. The highest emissivity could be achieved with OT13, however, after 10 h aging the values were much lower. Both the values before and after aging are not typical for oxide ceramics, which usually decrease with increasing temperature in the range 0,3 to 0,6. The high values are achieved by a special treatment of the coatings. The best stability has the STZ-coating which therefore is now favored because it assures high emissivity during the expected lifetime of the x-ray anode.

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

### 3.2 Oxidation protection coatings for re-usable space transport systems

C/SiC composites are generally established as the most appropriate materials to protect space transport systems during atmospheric reentry. Results of the uncoated material produced by the German Aerospace Research Establishment, DLR, Stuttgart have been published earlier [11]. Two types of coatings have been investigated in the frame of a programme of developing oxidation protection of C/SiC composites.

a) SiC-layers were 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 coating 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 into a solution of the corresponding polysilazane with toluene into which Si or SiC in form of powder with particle diameters of 3,6 mm (Si) or 0,4 mm (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, (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 of Si is leading 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 neglectible. 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 indicating that $SiO_2$ was formed at the surface whereas the spectral emissivity of (Si-C-N) + Si are more or less constant in the range 0.85. In Fig. 7 the spectral emissivity of (Si-B-C-N) + Si is plotted which is practically identical with (Si-B-C-N) + SiC (not presented) and the curves of (Si-C-N) + Si in Fig. 6.

Taking into account the radiation properties, 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 are not yet completed. Reentry tests with SiC-coatings are described in the next chapter.

3.5 Emissivity measurements before and after atmospheric reentry tests

Thermal protecting materials of re-usable space transport systems are exposed to very high heat fluxes ranging up to 1,8 $MW/m^2$. The maximum temperatures reached during the reentry is in the order of 2000°C to 2100°C. Material specimens of C/C-SiC composites, produced at DLR, Stuttgart using the liquid silicon infiltration process (LSI) could be tested on Russian FOTON capsule reentry flight experiments in 1994 [14]. Two types of specimens were used:

a) C/C-SiC uncoated

b) C/C-SiC coated with SiC by multilayer CVD coating with a total thickness of 98 mm.

The reason of the coating was twofold: protection of the material against oxidation and increase of the emissivity. Fig. 8 and 9 show the total and spectral emissivity results. The decrease of the spectral emissivity with wavelength of the uncoated, virgin material has been explained

earlier in [15] by the contribution of the surface structure of the carbon fibers (T800). This behavior of the spectral emissivity and the Wien's displacement law are the reason for the increase of 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 again the emissivity

a) FOTON F3: CVD-SiC coated, after one mission

b) FOTON F6: uncoated C/C-SiC, after two missions

The CVD-coating at sample F3 completely disappeared and the total emissivity is now 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 combination with surface mapping by means of energy dispersive x-ray analysis (EDX) deliver the explanation.

The hypothesis of the principal damaging process is given in [14] as follows:

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

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

If we compare the EDX pictures of the F3 and F6 specimens we find approximately 40% $SiO_2$ and 40% SiC and practically no C, whereas F6 shows 30% $SiO_2$, 30% SiC and 30% C. 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 fiber structure with low emissivity in the infrared. The total emissivity thereby increased in a similar degree as at F6 after the second mission. Only in the visible the spectral emissivity is lower, Fig. 10 and similar to the values of F3, what explains, that the visual impression of both materials is nearly the same. The decrease of the total emissivity of F3 corresponds with the variation of the spectral emissivity with wavelength and the 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 has to be expected, resulting from the kind of material preparation, the thermal treatment and the chemical

reactions on the surface. Predictions are thereby very difficult, especially if oxidation takes place leading here to a reduction of the emissivity in the visible and near infrared, in contrary to metal surfaces the emissivity of which increases by oxidation. As known from the literature even small impurity contents in a pure oxide ceramic may lead to a drastic variation of 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 additionally complicates the situation.

On the other side measurements are difficult in the high temperature range. Therefore it would be important to compare measurements carried out at several different laboratories. For that purpose specimens are needed which are stable with regard to its emissivity and which can be prepared with reproducible surface. During our measurements we tried to select a number of candidate materials which shall be included in a planned round robin programme of a couple of laboratories. In the high emissivity range SiC (bulk material or coating) and graphite (isotropic, special surface treatment) has been stated in [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 Rhodium content was varied between 0 and 40 vol% without remarkable influence on 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 field. The results of our preliminary measurements are presented in Fig. 11 and 12.

## 5. ACKNOWLEDGMENT

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Tab. I Chemical composition of the x-ray anode coatings [10]

| | $SiO_2$ (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 |

**FIGURE CAPTIONS**

Fig. 1 Total and spectral emissivity measurement device

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

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

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

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

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

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

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

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

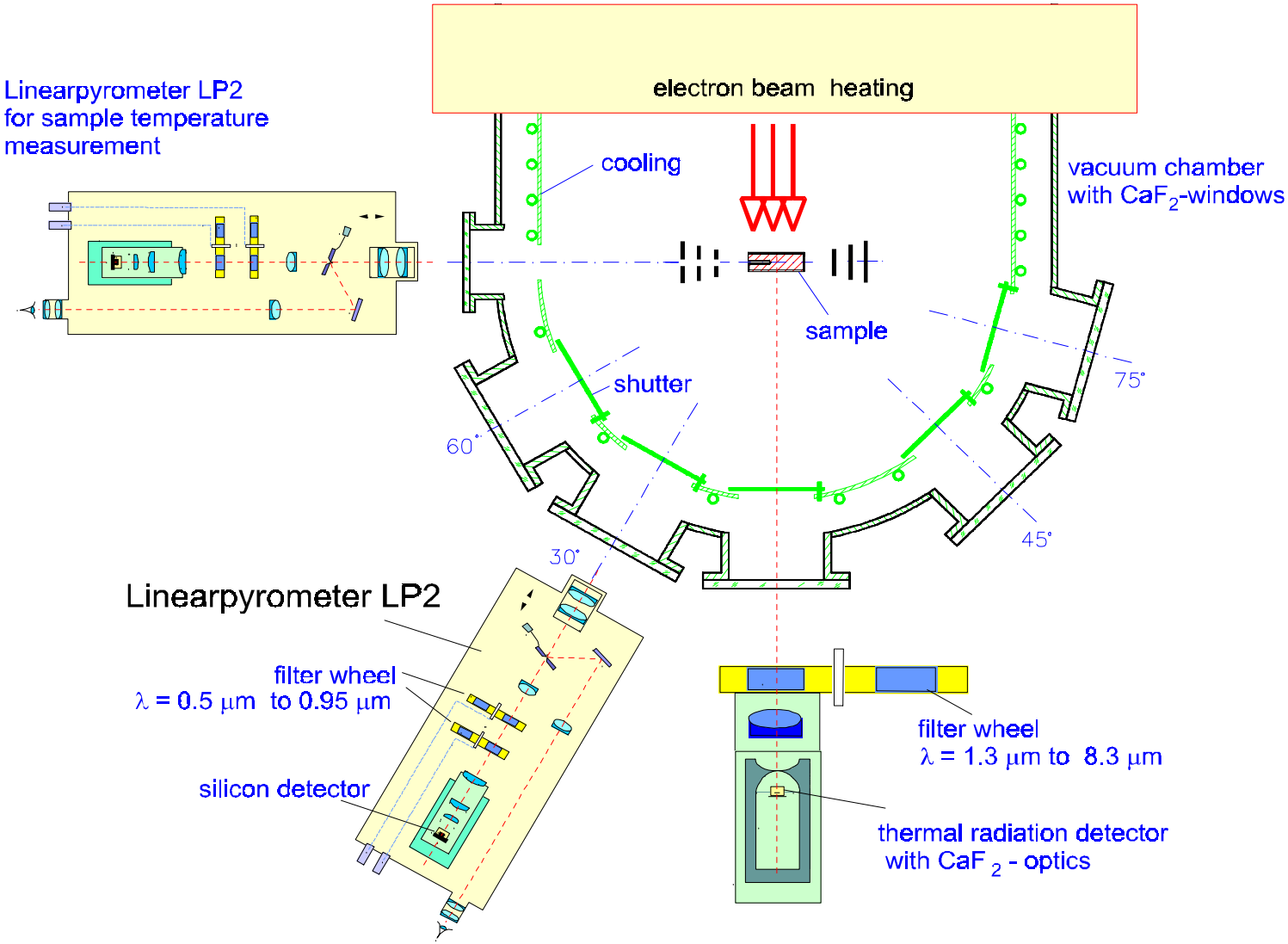


Fig.1 : Neuer, Jaroma-Weiland

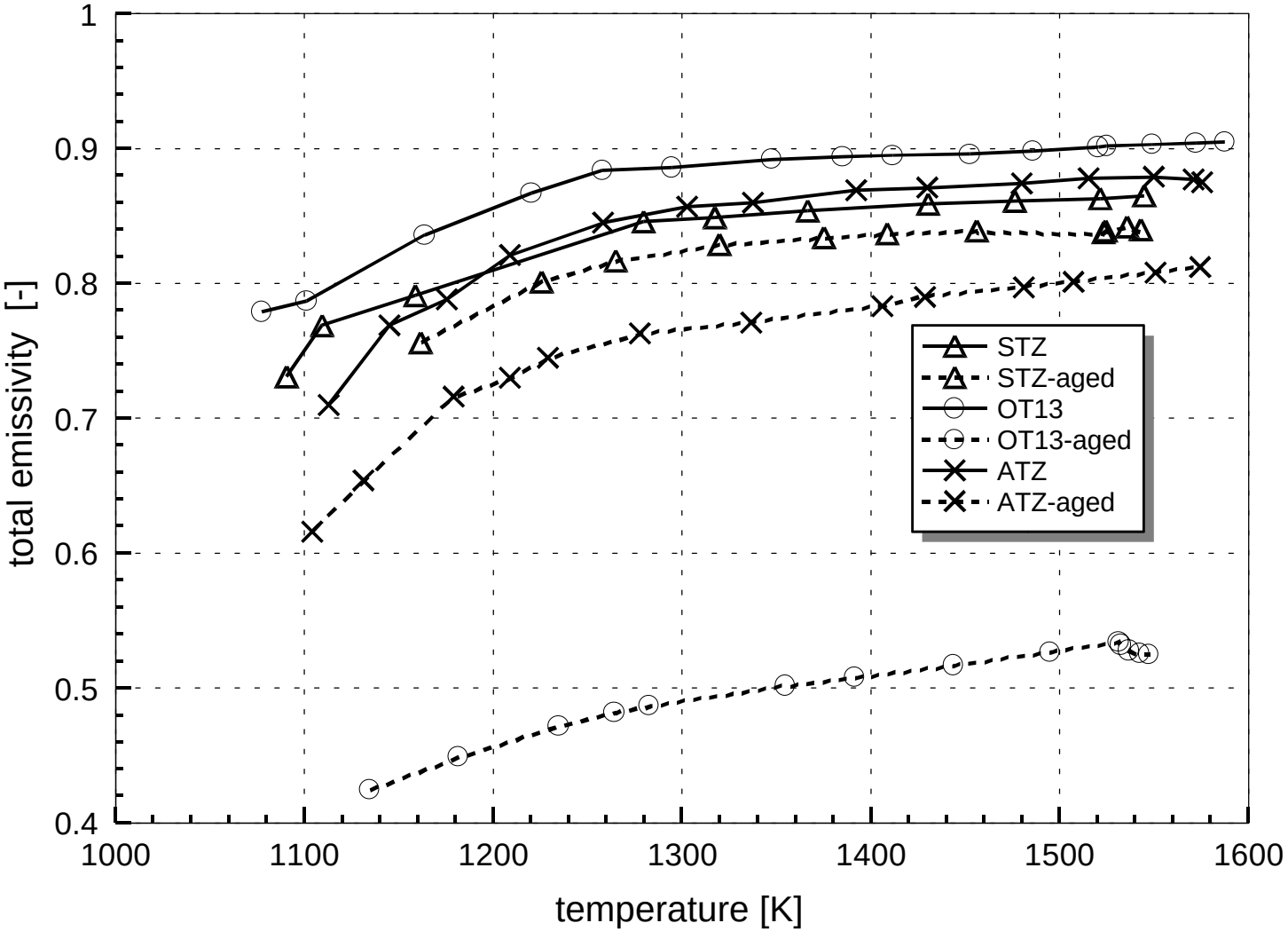


Fig.2: Neuer,Jaroma-Weiland

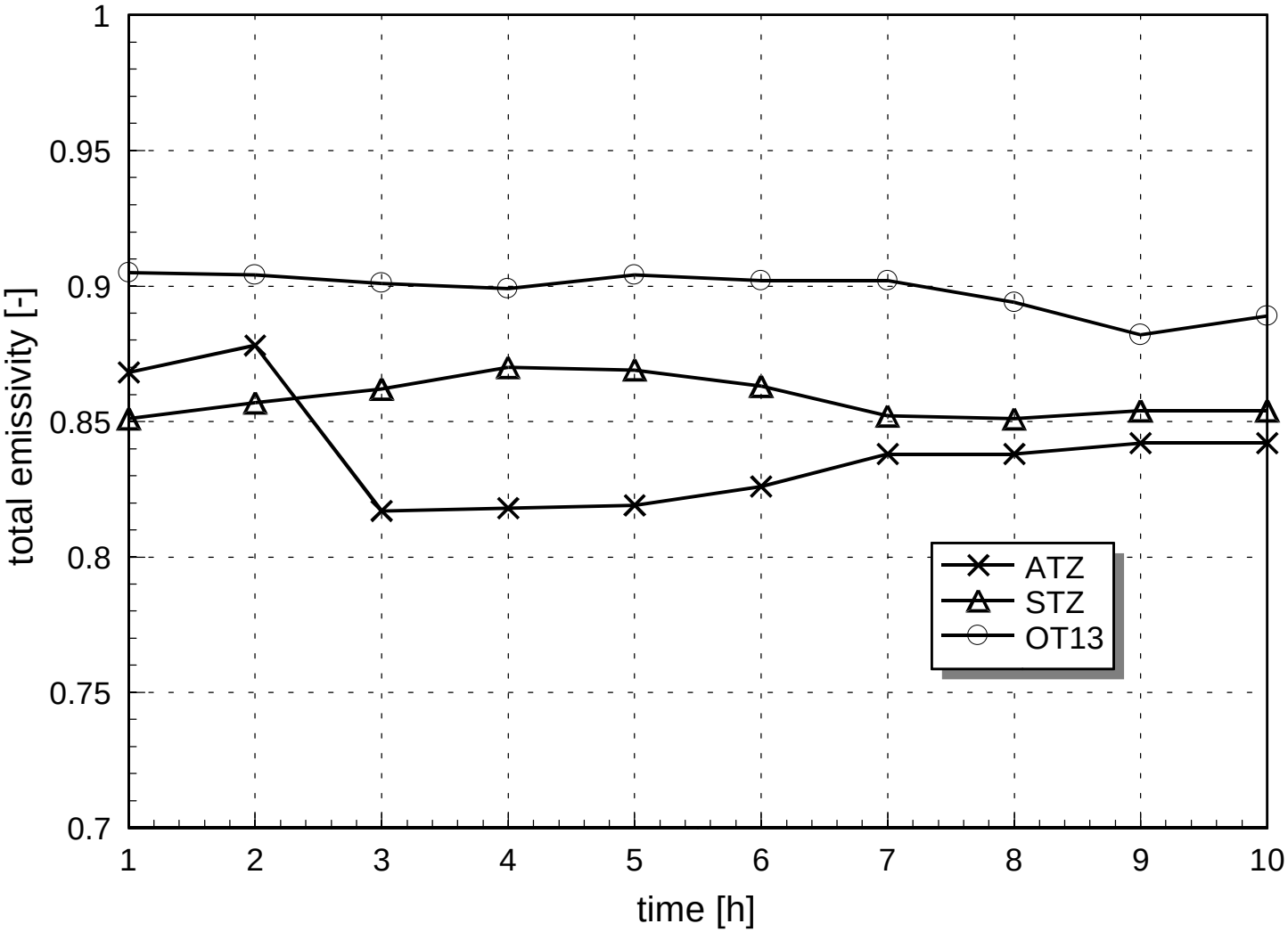


Fig.3 Neuer, Jaroma-Weiland

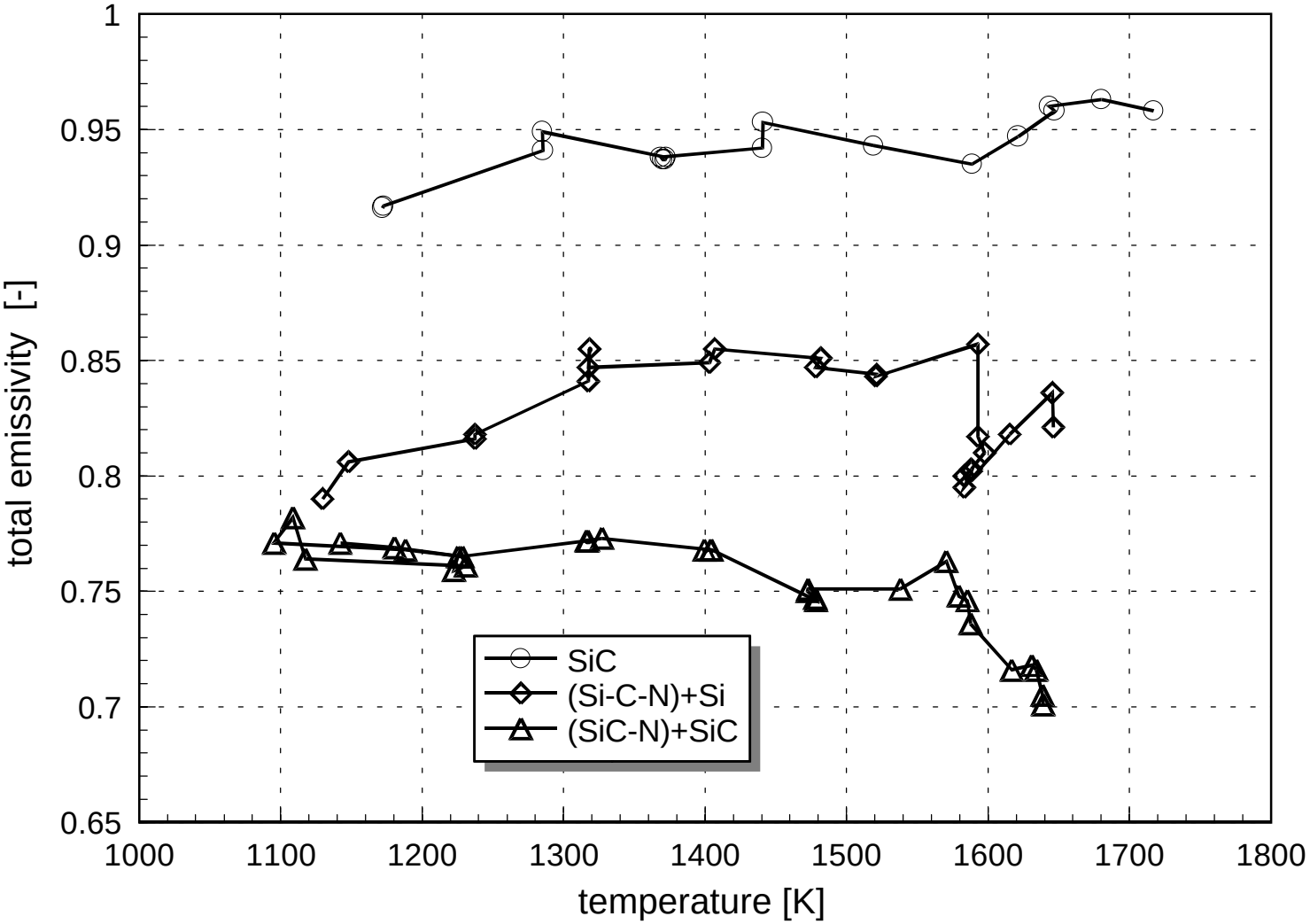


Fig.4; Neuer, Jaroma-Weiland

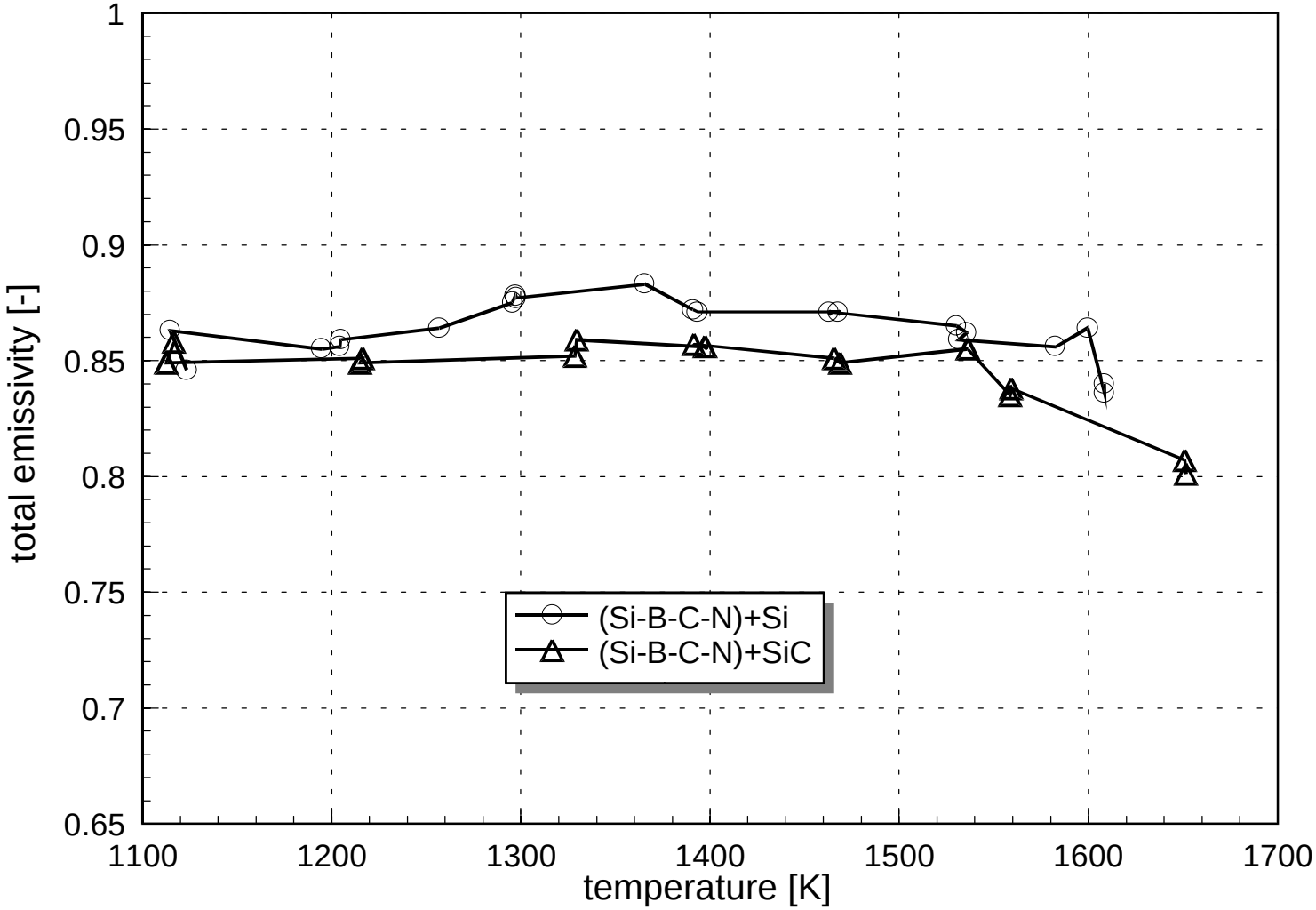


Fig.5; Neuer,Jaroma-Weiland

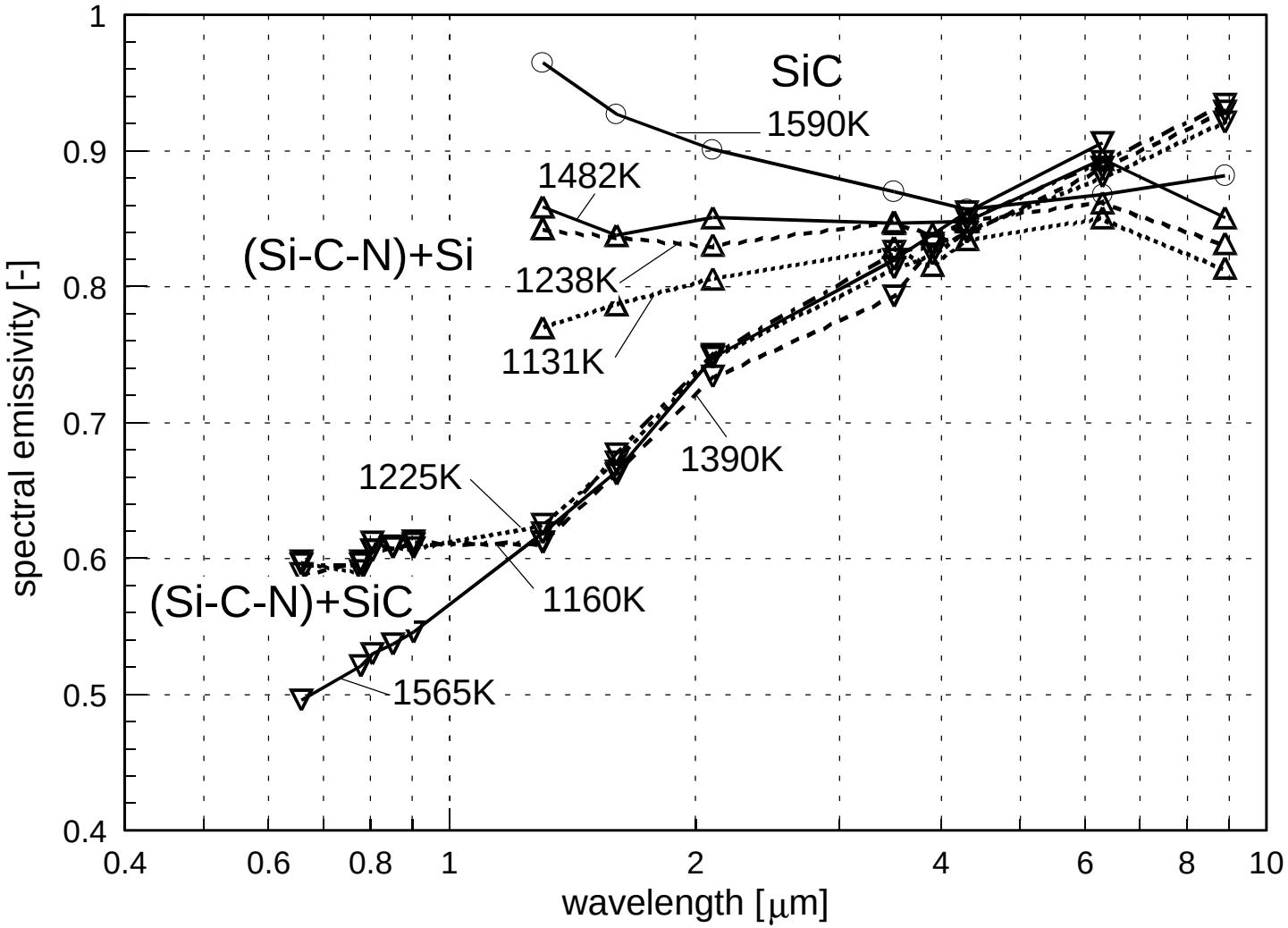


Fig.6: Neuer,Jaroma-Weiland

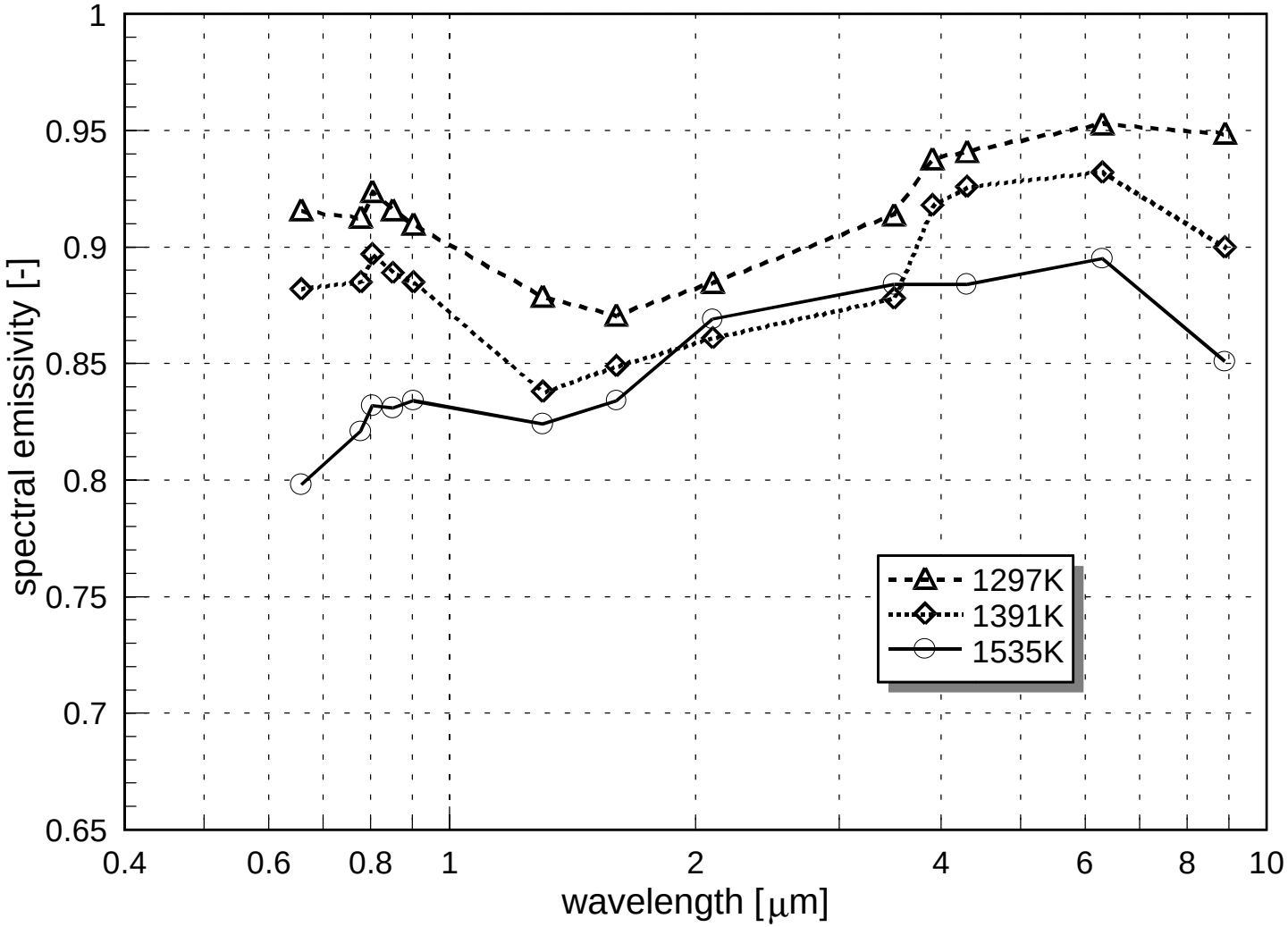


Fig.7; Neuer,Jaroma-Weiland

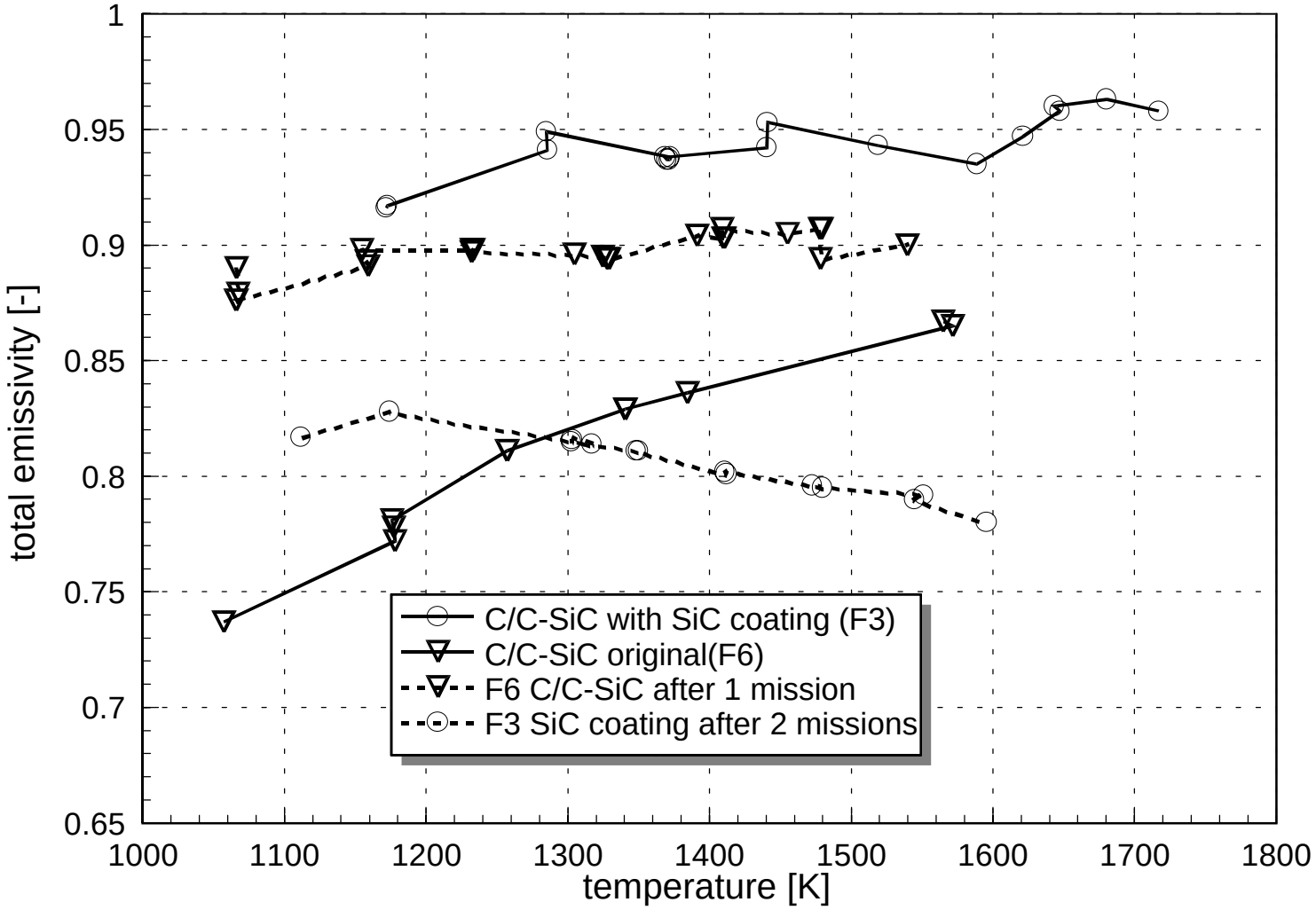


Fig.8 Neuere, Jaroma-Weiland

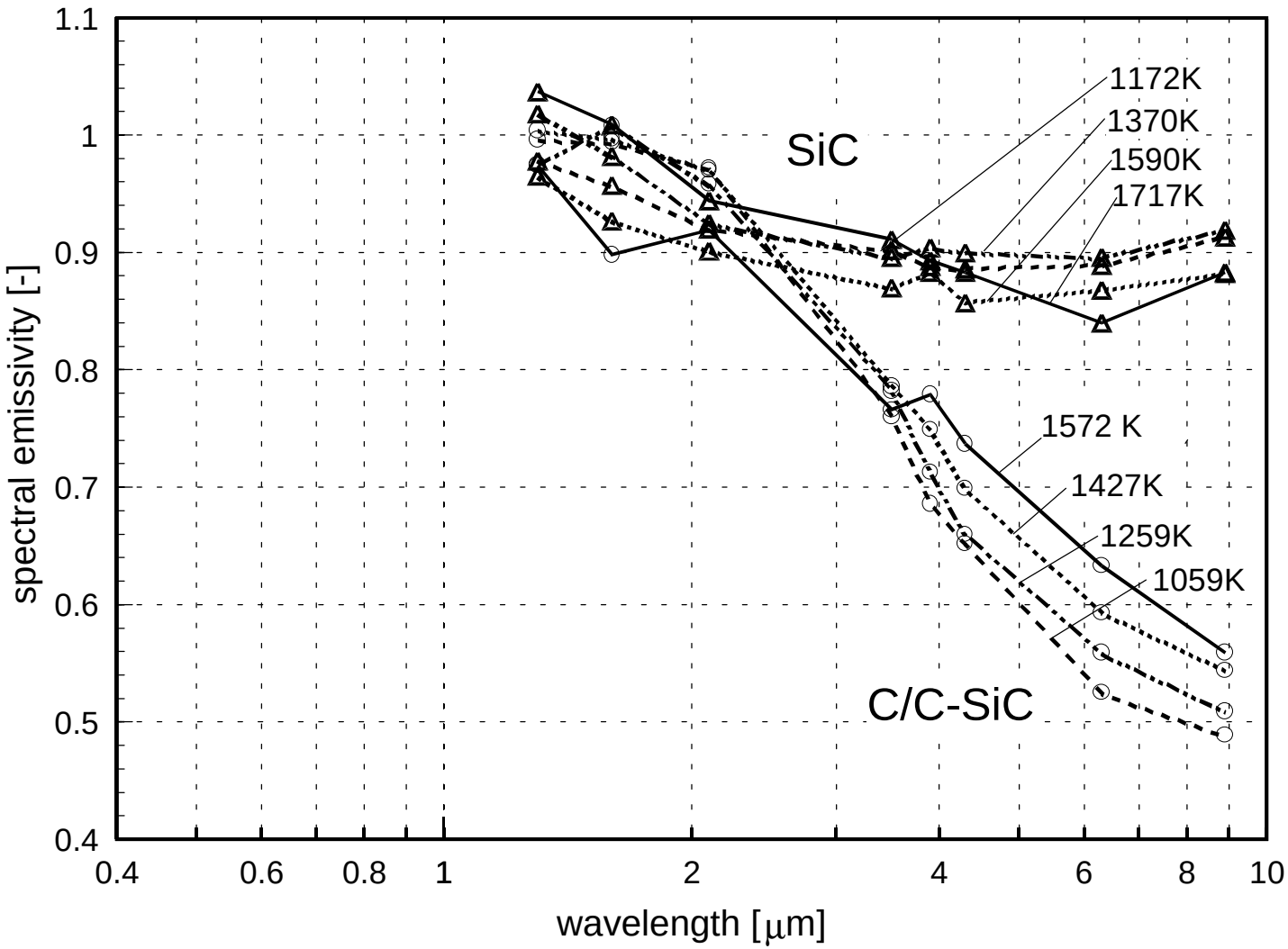


Fig.9 Neuer,Jaroma-Weiland

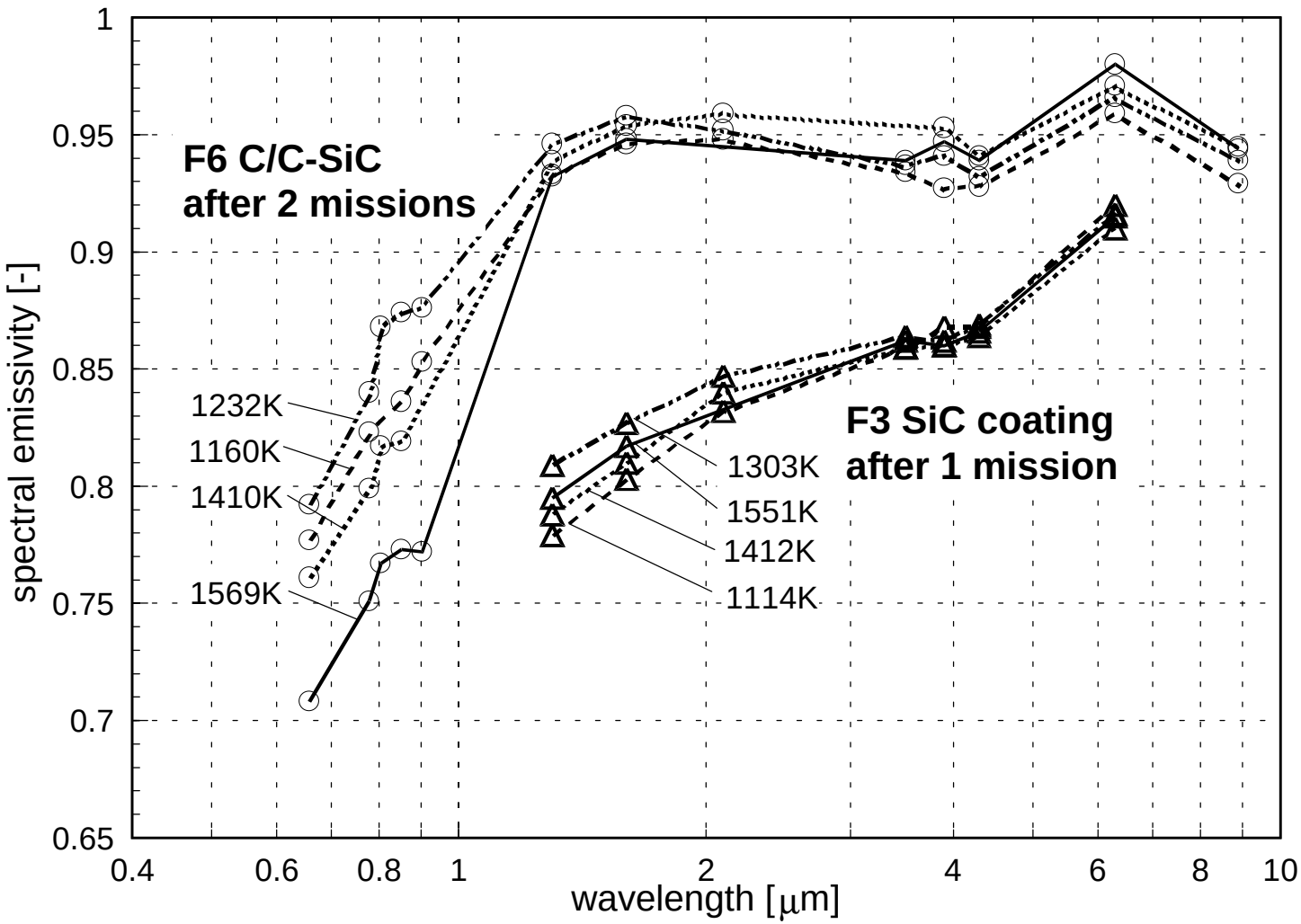


Fig.10 Neuer, Jaroma-Weiland

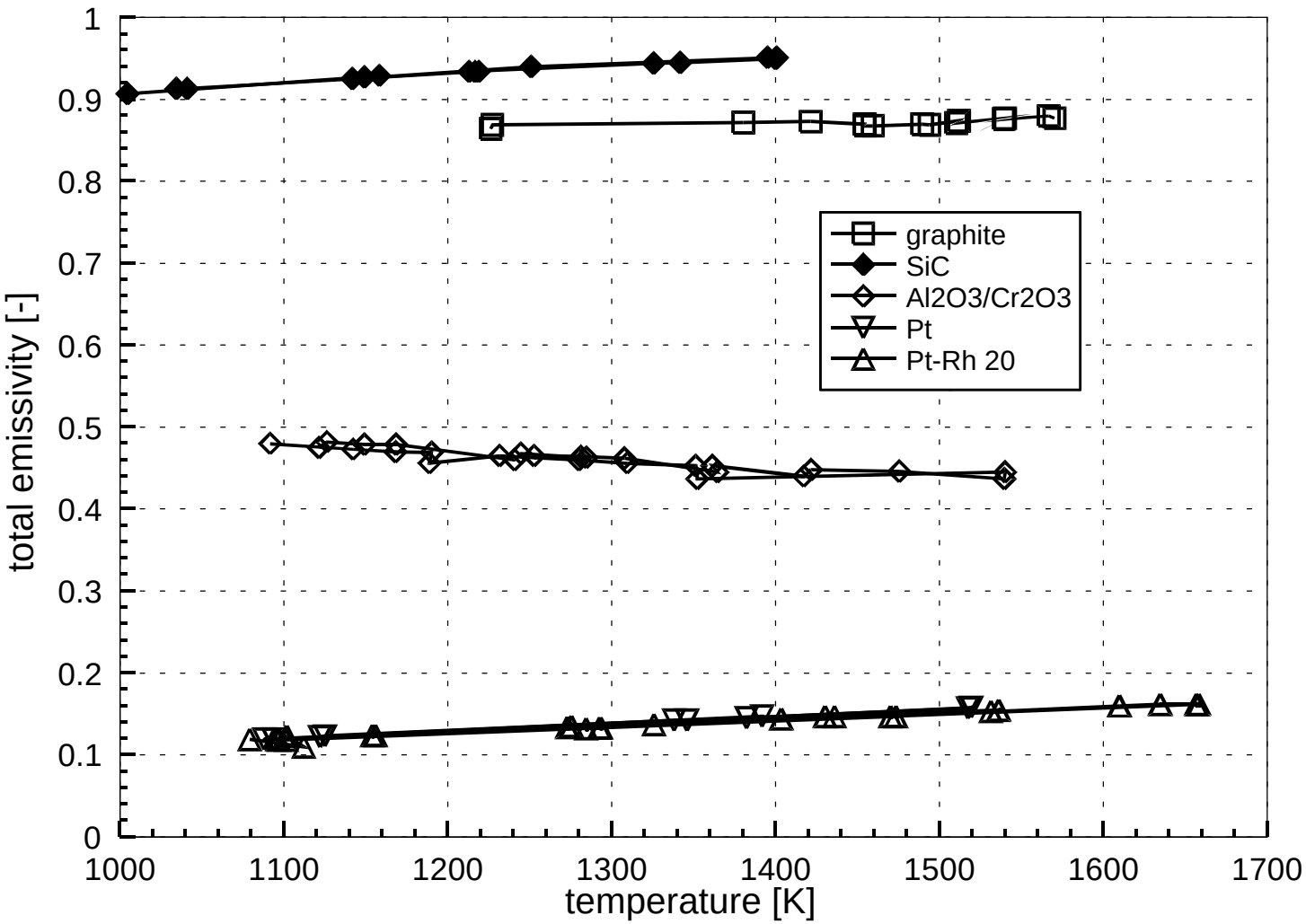


Fig.11: Neuer,Jaroma-Weiland

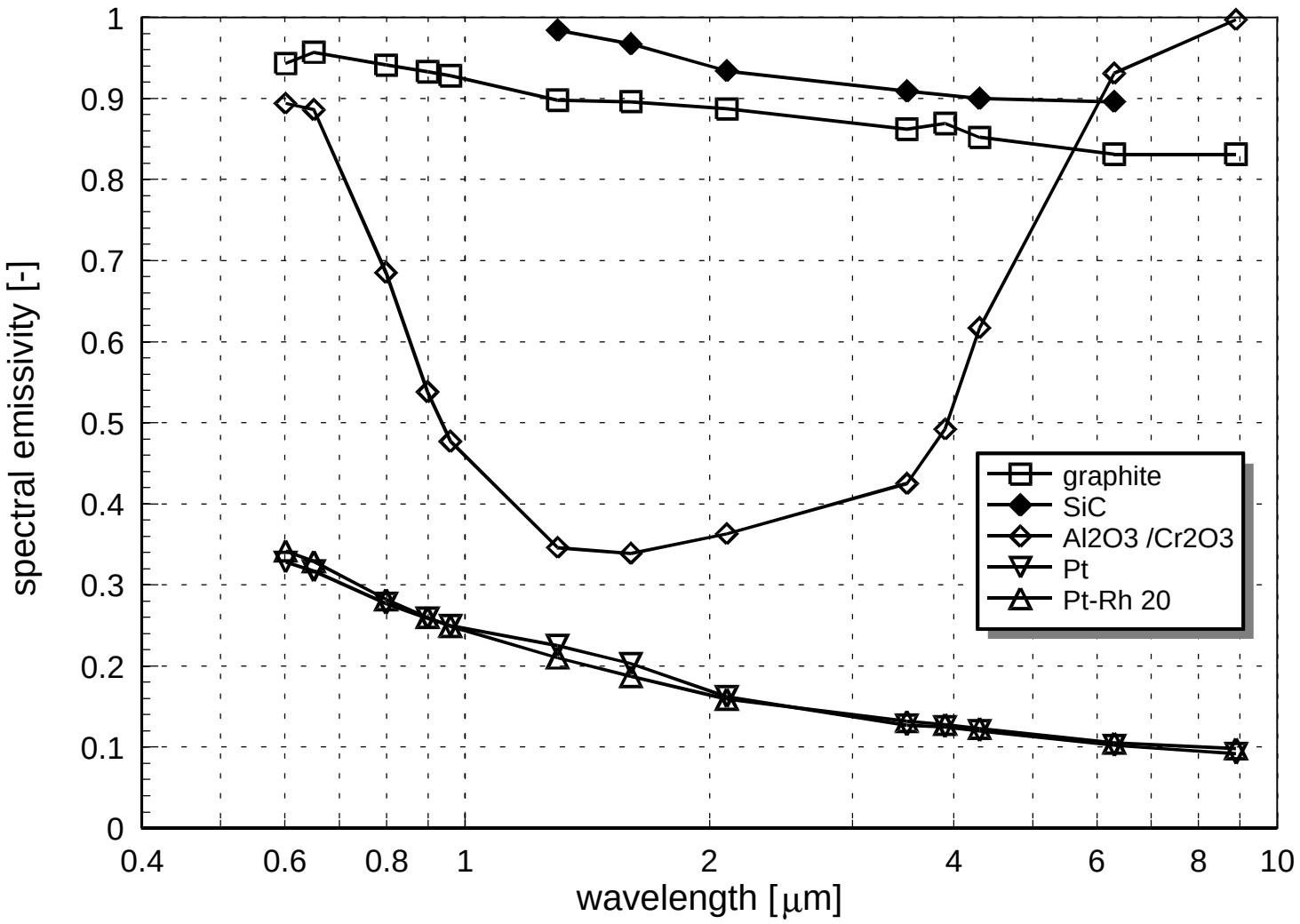


Fig.12; Neuer,Jaroma-Weiland