Zircaloy Emissivity

Recommendation

Above 800 K, the recommended values for the total emissivity of oxidized Zircaloy-4 are values obtained by Mathew, Evans, Heinrichs, and George [1] from their extensive measurements during steam oxidation in the temperature range 1423-1923 K. Their measurements showed that the emissivity of the substoichiometric, black oxide is a constant value in the range of 0.82 to 0.85 and the emissivity of the white oxide layer ranges from 0.78 to 0.80. These values obtained from 1423-1923 K are recommended at lower temperatures because of their good agreement with measurements on white and black oxides from 860-1530 K by Kovalev and Melnikov [2] and with measurements by Burgoyne and Garlick[3] as a function of oxide thickness in the 650-1100 K temperature range.

The recommendation for the emissivity of unoxidized Zircaloy-4 from 1350 to 1900 K is based on the more than 1700 measurements of Mathew et al. [1], which showed that the emissivity in this temperature range varies from 0.18 to 0.20. These data and the Zircaloy-2 data from 373-573 K, obtained by Murphy and Haveloch [4], have been fit to obtain an equation for unoxidized Zircaloy (both Zircaloy-2 and Zircaloy-4) from room temperature to 1900 K.

For 373 K < T < 1900 K,

$$\varepsilon = 0.1906 - 0.2166 \ \exp(-3.792\, x 10^{-3}\ T)\,; \tag{1}$$

where

ε is the total emissivity of unoxidized Zircaloy

T is the temperature in K

An exponential form of equation was chosen to provide the constant value of 0.19 at temperature above 1350 K in accord with the approximate constant variation in the data of Mathew et al.[1]. It should be noted that the emissivity of unoxidized Zircaloy-4 depends on the surface conditions of the material.

The recommended equation for the emissivity of Zircaloy as a function of oxide thickness and temperature was obtained by a constrained least squares fit of the data [1, 3-5]. This fit included the constraint that at 0 oxide thickness, the emissivity equation reduces to Eq.(1) for unoxidized Zircaloy.

For 373 K < T < 1973 K

$$\varepsilon = 0.1906 - 0.2166\ \exp(-3.792\ x10^{-3}\ T) + 0.6193[1 - \exp(-0.6186\ x)]; \qquad (2)$$

where

ε is the total emissivity of Zircaloy

T is the temperature in K

x is the thickness of the oxide layer in μm (10^{-6} m)

At temperatures equal or greater than 1423 K and an oxide thickness greater or equal to 10 μm, Eq.(2) gives a constant value of 0.81, which is the average of values of the emissivity of black and white oxides reported by Mathew et al.[1].

Uncertainty

The recommendations for the total emissivity of Zircaloy-4 with a substoichiometric black oxide coating and a white oxide coating includes the experimental uncertainty in the range of the values given. It is about 3%. The uncertainty for Eq.(2), the recommended equation for Zircaloy as a function of oxide thickness (including unoxidized Zircaloy) is 10%, which is the scatter in the data.

Discussion

Review of Data on Unoxidized Zircaloy

Data for the emissivity of unoxidized Zircaloy are listed in Table 1 and shown in Figure 1. The circles at 0.19 with error bars of ±0.1 represent the more than 1700 Zircaloy-4 emissivity measurements of Mathew et al.[1]. These measurements indicated that the emissivity of Zircaloy-4 from 1350 to 1900 K is a constant between 0.18 and 0.20.

Measurements from 1218 to 1472 K made by Jeunke and Sjodahl also indicated that the Zircaloy emissivity is a constant but that the value is around 0.24. Earlier measurements by Lemmon [6] and by Lucks et al. [7] showed an increase in emissivity with temperature. It should be noted that the emissivity of unoxidized Zircaloy-4 depends on the surface conditions of the material. Because the more recent and more precise measurements indicate no increase with temperature above 1200 K, the data of Lemmon and that of Lucks et al. have not been included in the final analysis. The data of Mathew et al. are preferred to that of Jeunke and Sjodahl because of their larger number of measurements, and larger temperature range. Thus the results of Mathew et al. are recommended for the emissivity of unoxidized Zircaloy from 1350 to 1900 K.

Table 1 Unoxidized Zircaloy Emissivity Data

Experimenter	Year	Temperature ,K	Sample	Direction Measured
Mathew et al. [1]	1994	1356-1903		more than 1700 data
Murphy & Haveloch [4]	1976	373 – 673	Pickeled	Normal, Hemispherical
		423 - 473	Rough	
Jeunke & Sjodahl [5]	1968	1218 – 1472		
Lemmon [6]	1957	1334 – 2041	S1	Normal, Hemispherical
		1249 – 2016	S2	Normal, Hemispherical
		1329 - 1940	S3	Normal, Hemispherical
Lucks et al.[7]	1956	1274 - 1976	S1	Normal, Hemispherical
		1475 - 2026	S2	Normal, Hemispherical
		1475 - 2026	S3	Normal, Hemispherical

The only low temperature data available for unoxidized Zircaloy are the Zircaloy-2 data of Murphy and Haveloch [4]. Figure 1 shows that three normal emissivity data of the pickeled sample of Murphy and Havelock at 423 and 673 K are high and the 673 K hemispherical emissivity datum of the pickeled sample of Murphy and Havelock is also high. These three data have not been included in this analysis.

The remaining data of Murphy and Haveloch and the data of Mathew et al. have been fit to an equation with an exponential temperature dependence. An exponential form was chosen for this least squares fit so that the equation would go to a constant at high temperatures, as indicated by the measurements of Mathew et al. Figure 2 shows the recommended equation, Eq.(1), with the data fit. In the figure, the more than 1700 data of Murphy et al. are represented by circles at 0.19 every 20 K. The recommended equation, Eq.(1), fits the data with a standard deviation of 8.8×10^{-5}. Thus the uncertainty in the recommended equation is given by the maximum scatter in the data, which is 10%.

Review of Data on Oxidized Zircaloy

Data for the total emissivity of oxidized Zircaloy from measurements listed in Table 2 are shown in Figure 3. The data of Lemmon [6] and the data of Lucks et al.[7] are inconsistent with all the other data above 1200 K. Their measurements were made in a vacuum, which may have caused the oxide layer to dissolve resulting in a decrease in emissivity with experiment duration. For these reasons, those data have not been included in this analysis.

New data published since the analysis given in MATPRO [8] are the AECL data of Mathew et al.[1] and the data of Kovalev and Melnikov [2]. Figure 3 shows that these data for a black sub-stoichiometric oxide are consistent with the data of Burgoyne and Garlick [3] and the data of Jeunke and Sjodahl [5] at 1375 and 1475 K but are higher than the Jeunke and Sjodahl data at 1575 K. The MATPRO discussion of the data of Jeunke and Sjodahl states that the emissivity values observed by Jeunke and Sjodahl at 1575 K are consistent with oxidized clad that has undergone film boiling creating a spalled white oxide [8]. However, the 1575 K data of Jeunke and Sjodahl are inconsistent with both the white oxide layer data of Mathew et al. and the white oxide data of Kovalev and Melnikov. Note that the white oxide data of Mathew et al. and of Kovalev and Melnikov are consistent with the lower temperature data of Jeunke and Sjodahl and the uniform oxide data (10 and 28 μm) and nodular oxide data of Burgoyne and Garlick [3].

Table 2 Measurements of Emissivity of Oxidized Zircaloy

Experimenter	Year	Temperature K	Comments
Mathew et al. [1]	1994	1423-1973	black and white oxide after exposure to steam
Kovalev & Melnikov [2]	1979	860-1530	black & white oxide
Burgoyne & Garlick [3]	1976	735 – 1080	uniform oxide 10, 28 μm
		654 – 1149	nodular oxide 130 μm
		677 – 977	crud thickness:35 μm, not included in fit
Murphy & Havelock [4]	1976	373 – 673	normal & hemispherical in steam; thickness: 0.46, 1.1, 1.8, 2.0 μm
Jeunke & Sjodahl [5]	1968	1125 - 1575	In steam & vacuum, calculated thickness: 17 – 125 μm
Lemmon [6]	1957	1239 -2039	Measurements in vacuum, Oxygen content 1.8-3.6% Not included in analysis
Lucks [7]	1956	1274 - 1976	Measurements in vacuum, Oxygen content 0.14 – 0.57% Not included in analysis

In Figure 4, emissivity as a function of time exposed to steam reported by Mathew et al. [1] and by Mathew and George [1] are compared with data of Jeunke and Sjodahl [5]. The 1575 K data of Jeunke and Sjodahl are significantly lower than their data at other temperatures and with the higher temperature data of Mathew and George. Thus, the 1575 K data of Jeunke and Sjodahl have not been used in determining an equation as a function of thickness of the oxide layer.

Comparison with MATPRO Equations

The equations recommended in the MATPRO manual [8] were obtained from analysis of the normal emissivity data of Murphy and Haveloch [4], data of Burgoyne and Garlick [3] and the data of Jeunke and Sjodahl [5]. The MATPRO equations are:

For T < 1500 K and an oxide layer thickness < 3.88 μm (1 μm = 10^{-6} m)

$$\varepsilon_1 = 0.325 + 0.1246\ x\ 10^6\, d\ ; \tag{3}$$

For T < 1500 K and an oxide layer thickness $\geq$ 3.88 μm,

$$\varepsilon_1 = 0.808642 - 50.0\ d\ ; \tag{4}$$

where

ε_1 = total emissivity (either normal or hemispherical)

d = oxide layer thickness in m.

For T> 1500 K, the larger of either

$$\varepsilon_2 = \varepsilon_1\ \exp\left[\ \frac{1500 - T}{300}\ \right]; \tag{5}$$

or

0.325,

where ε_1 is defined by Eqs.(3-4) depending on oxide thickness.

The value 0.325 is an estimate of the minimum emissivity of ZrO_2. The estimate of the minimum emissivity of ZrO_2 was based on the assumption, made by Juenke and Sjodahl, that at 1575 K, the emissivity of the oxide film approached the emissivity of ZrO_2.

In Figure 5, the MATPRO recommendations for oxide thicknesses of 2 and 10 microns are compared with available data as a function of temperature. Above 1500 K, the MATPRO recommendations decrease with temperature to emissivity values in the range of the data of Lemmon [6] and of Lucks et al. [7], which are unreliable because of their reducing conditions and which disagree with the data of Mathew et al.[1] and the data of Kovalev and Melnikov [2]. In Figure 6, values calculated with the MATPRO equations (3-5) for temperatures below 1500K, 1575 K, and 1973 K are compared with the available data as a function of oxide thickness. Although the MATPRO curve for emissivity as a function of oxide thickness for temperatures below 1500 K is consistent with the available data, values for 1973 K are far below the 1973 K data of Mathew et al.[1]. Consequently, the MATPRO equations are not recommended.

Analysis of Data on the Emissivity of Oxidized Zircaloy

Figure 3 shows that below 600 K, the emissivity of oxidized Zircaloy is an increasing function of temperature similar to that for unoxidized Zircaloy (Figure 2). If the Jeunke and Sjodahl at 1575 K and the data of Lucks et al. and of Lemmon in Figure 3 are excluded, the remaining high-temperature oxidized-Zircaloy emissivity data show very little variation with temperature. This is confirmed in Figure 7, which shows a bubble graph of the emissivity of oxidized Zircaloy as a function of oxide thickness in which the size of the bubble is proportional to the temperature. Note that the 5 µm datum at 1973 K of Mathew et al. is consistent with the 2.3 µm data of Murphy and Havelock and with the 10 µm data from 735-1072 K of Burgoyne and Garlick. The 94 µm data at 423 K of Murphy and Havelock are consistent with the 1473 K data of Jeunke and Sjodahl. The data of Bugoyne and Garlick at 35 µm appear high relative to other data at similar oxide thicknesses. In addition, it is not clear what the experimenters mean when describing this oxide as "crud". Thus these 35 µm data of Bugoyne and Garlick have not been included in the determination of the emissivity equation.

Figure 7 indicates very little variation in emissivity with oxide thickness at thicknesses greater than 5 µm. For thicknesses less than 5 µm, the emissivity decreases with decreasing oxide thickness. This behavior is that of an exponential function of oxide thickness. As the oxide thickness goes to zero, the Zircaloy emissivity must approach that for unoxidized Zircaloy. Thus, these data on emissivity as a function of oxide thickness have been fit to an equation with an exponential oxide thickness dependence with the constraint that at zero oxide thickness the emissivity is that of unoxidized Zircaloy given by Eq.(1). The temperature dependence is identical to that given by Eq.(1). Although Mathew et al. made many measurements of the emissivity of oxidized Zircaloy as a function of temperature, only 5 data are available as a function of oxide thickness. Therefore, the data of Mathew et al. as a function of oxide thickness have been weighted by a factor of ten in the least squares fit. The resulting equation, Eq.(2), fits the oxidized data with a standard deviation of 0.17 and all the data (oxidized and unoxidized) Zircaloy with a standard deviation of 0.003.

In Figure 8, the recommended equation for temperatures 423 K, 1000 K, and 1973 K are compared with the data for oxidized Zircaloy as a function of oxide thickness for thickness up to 100 μm. Figure 9 is a similar plot on a log scale in order to show more clearly the fit at low and high oxide thicknesses. Figure 10, which compares the Murphy and Havelock data for low oxide thicknesses with both the MATPRO equations and Eq.(2), shows that Eq.(2) fits these data somewhat better than the MATPRO equations.

The data for the emissivity of oxidized Zircaloy as a function of temperature are compared in Figure 11 with Eq.(2) for thicknesses of 0.9, 2, 5, and 10 μm. At thicknesses equal to or greater than 10 μm, Eq.(2) gives 0.81 for the emissivity of oxidized Zircaloy at temperatures equal to or greater than 1200 K. 0.81 is equal to the average of the emissivities of Zircaloy-4 with white (stoichiometric) and black (substoichiometric) oxides measured by Mathew et al. Thus, Eq.(2) is consistent with the data of Mathew et al. from 1423 to 1973 K. For temperatures from 1423 to 1973 K, the emissivity values obtained by Mathew et al. are recommended. The emissivity of Zircaloy-4 with white oxide layer is a constant, which ranges from 0.78 to 0.80. The emissivity of Zircaloy-4 with a sub-stoichiometric oxide black oxide is a constant in the range of 0.82 to 0.85.

References

1. P. M. Mathew, D. G. Evans, B. Heinrichs, and I. M. George, *Emissivity and Surface Colour of Steam-Oxidized CANDU Fuel Sheath at High Temperatures,* **AECL Report COG-93-486** (May 1994); see also P. M. Mathew and I. M. George, *Total Emissivity of Zircaloy-4 at High Temperatures,* Proc. 17th Annual CAN/CNS Conf. (1996).

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3. Burgoyne and Garlick, OECD-CSNI Meeting on the Behavior of Water Reactor Fuel elements under Accident Conditions in Spinad, Norway, Sept. 13-16 (1976), as tabulated and referenced in MATPRO, [Reference 8].

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6. A. W. Lemmon, Jr. *Studies Relating to the Reaction Between Zirconium and Water at High Temperatures,* **BMI-1154** (January 1957).

7. C. F. Lucks, G. B. Gaines, H., W. Deem, W. D. Wood, and W. E. Nexsen, Jr. USAEC Report **BMI-1094,** 84-86 (1956).

8. D. T. Hagrman, ed., MATPRO – A Library of Materials Properties for Light-Water-Reactor Accident Analysis,SCDAP/RELAP5/Mod 3.1 Code manual**, NUREG/CR-6150** Vol. 4 (1995).

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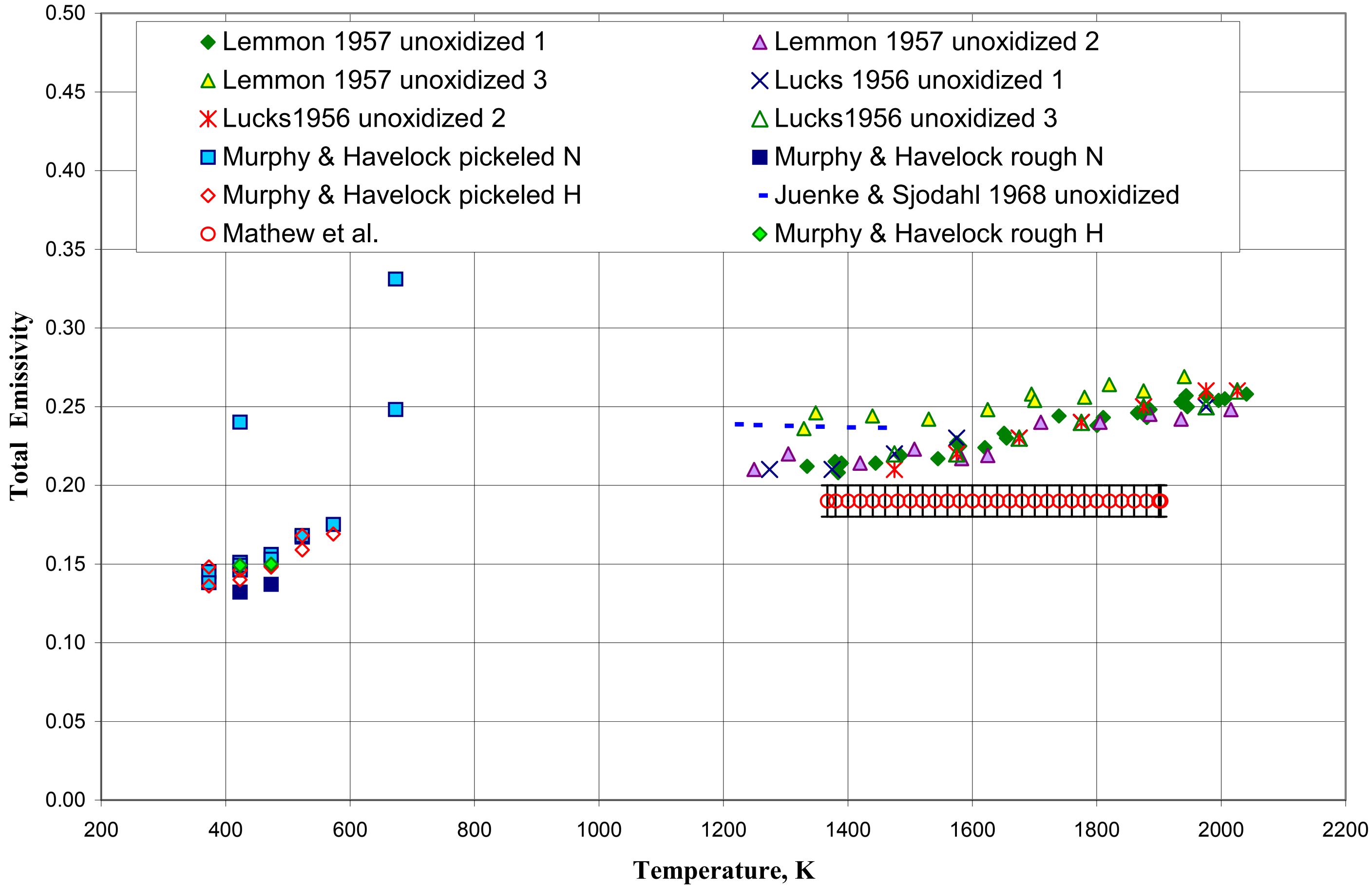

Fig. 1 Data for Emissivity of Unoxidized Zircaloy (H= hemispherical, N=Normal)

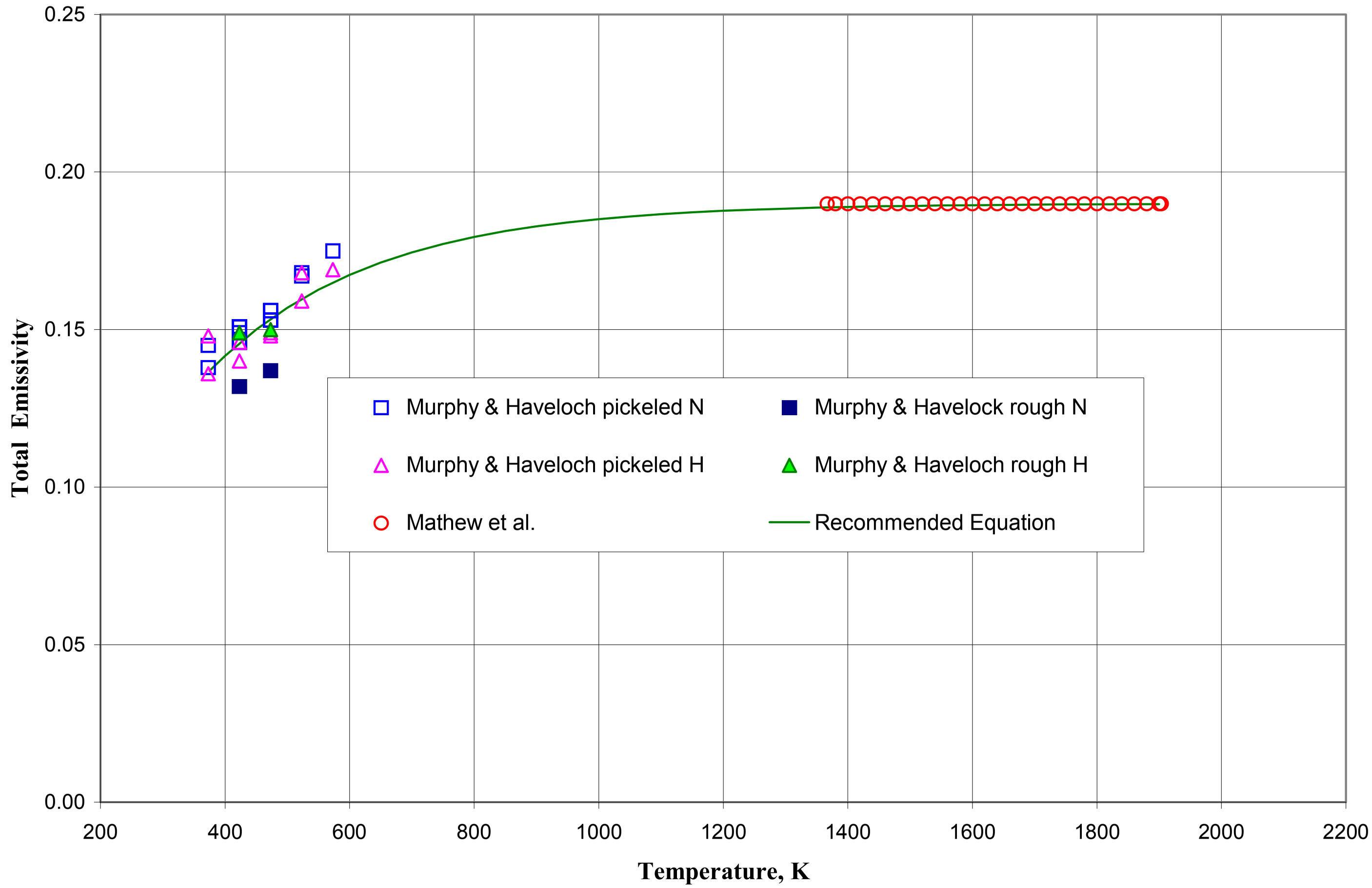

Fig. 2 Total Emissivity of Unoxidized Zircaloy (H=hemispherical, N=Normal)

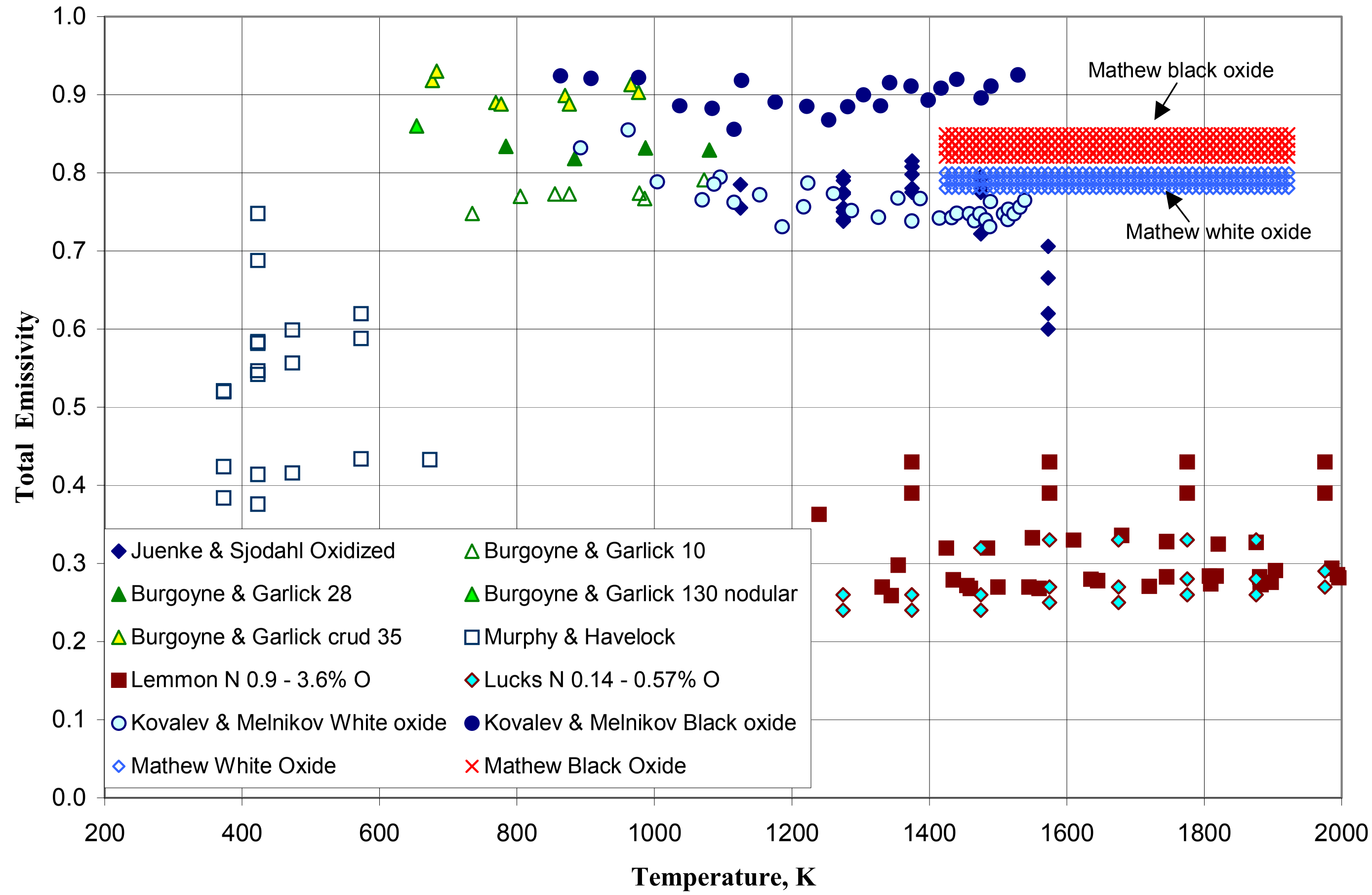

Fig. 3 Data for the Total Emissivity of Oxidized Zircaloy

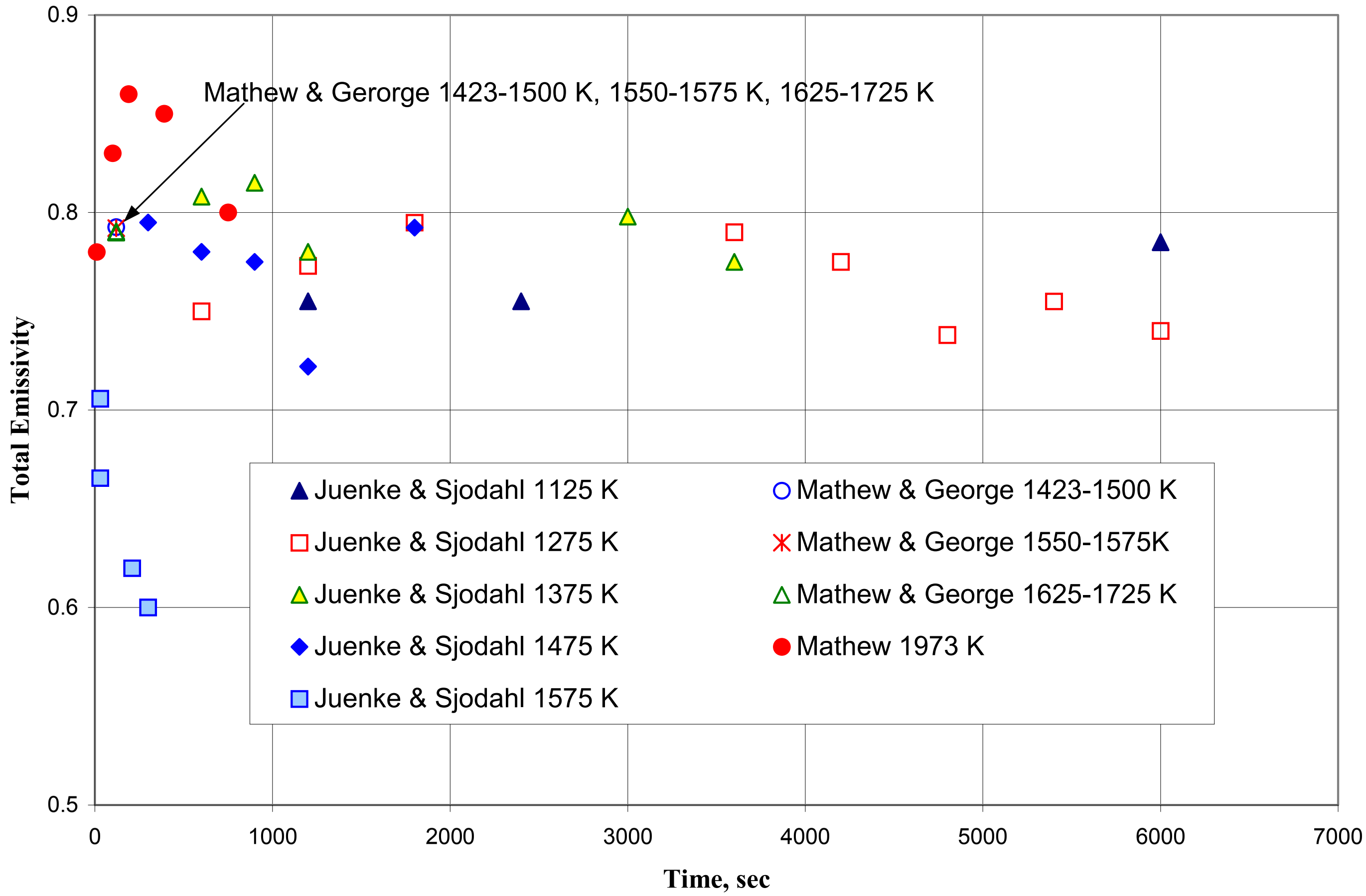

Fig. 4 Oxidized Zircaloy Emissivity as a Function of Time Exposed to Steam

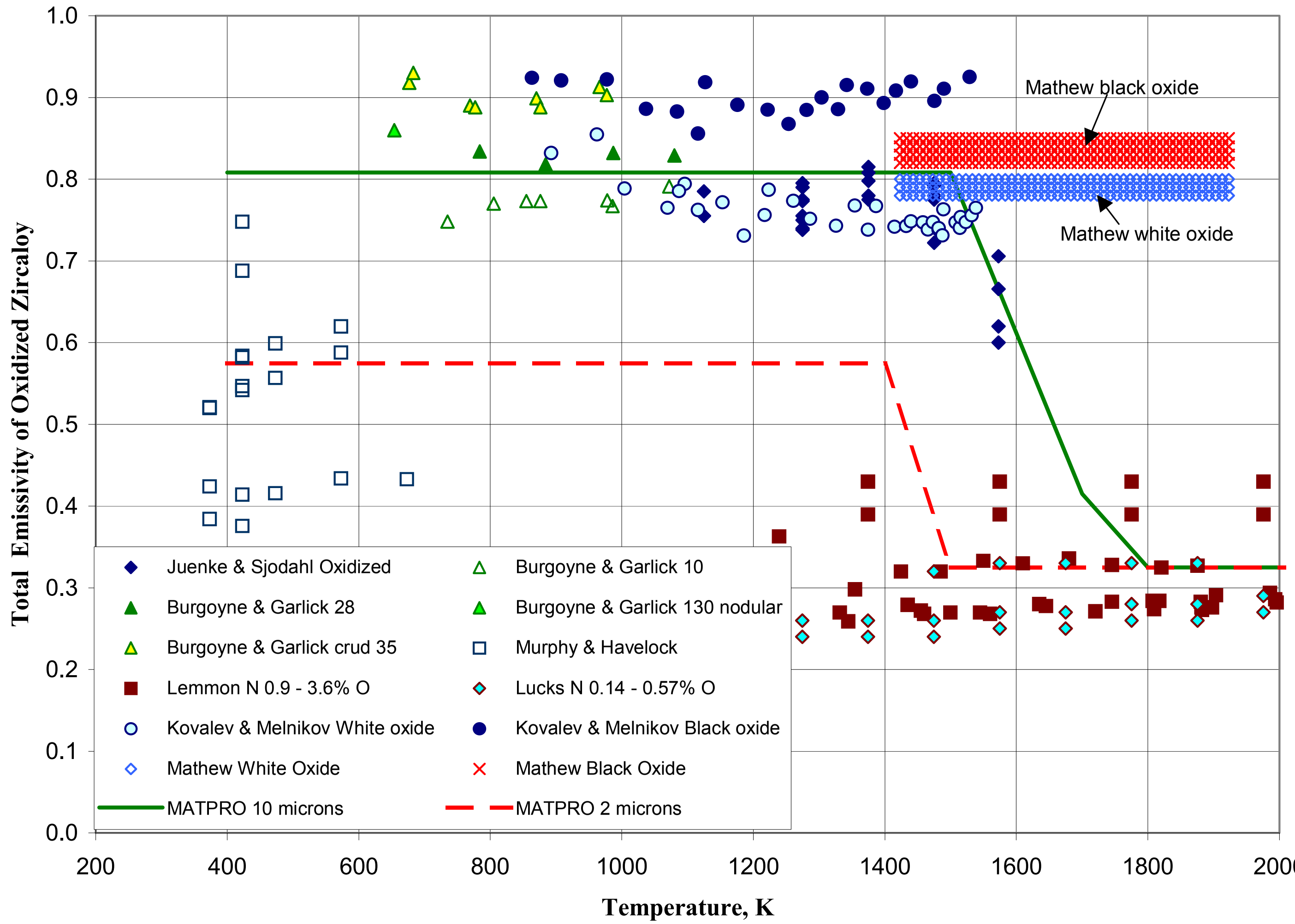

Fig. 5 Comparison of MATPRO Equations with Available Data

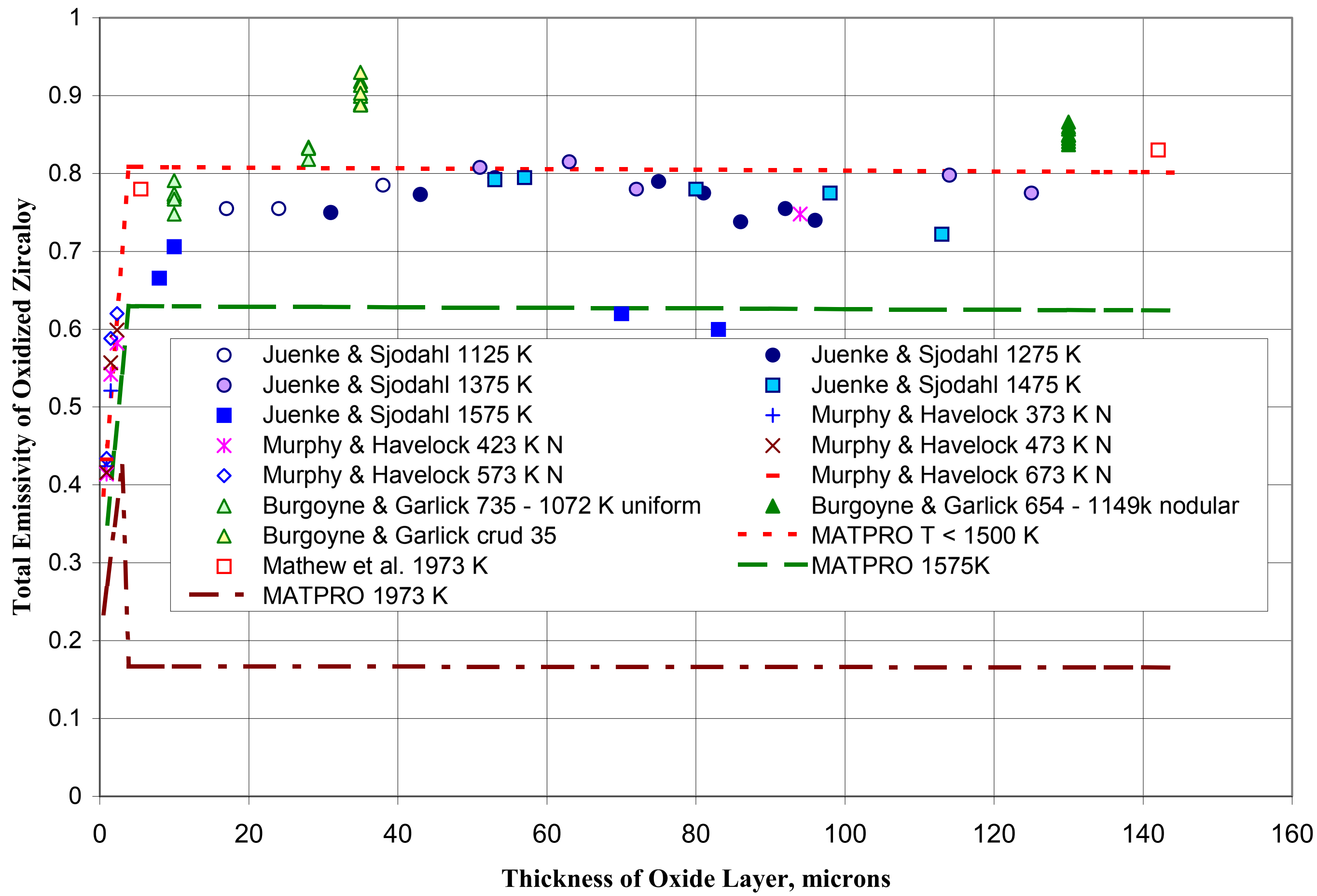

Fig. 6 Comparison of MATPRO Equations with Data as a Function of Oxide Thickness

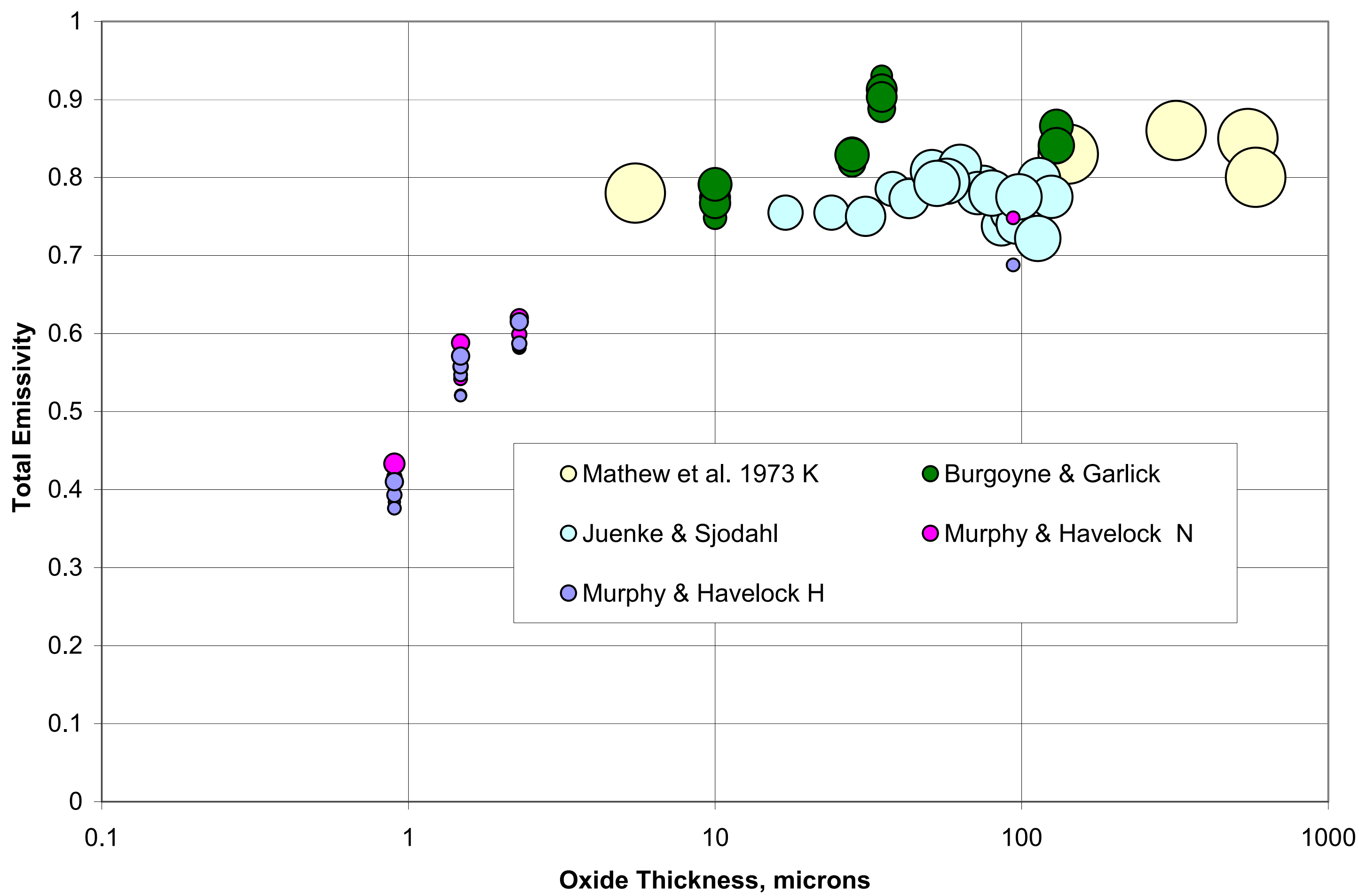

Fig. 7 Oxidized Zircaloy Emissivity as a Function of Oxide Thickness
Bubble Size is Proportional to Test Temperature

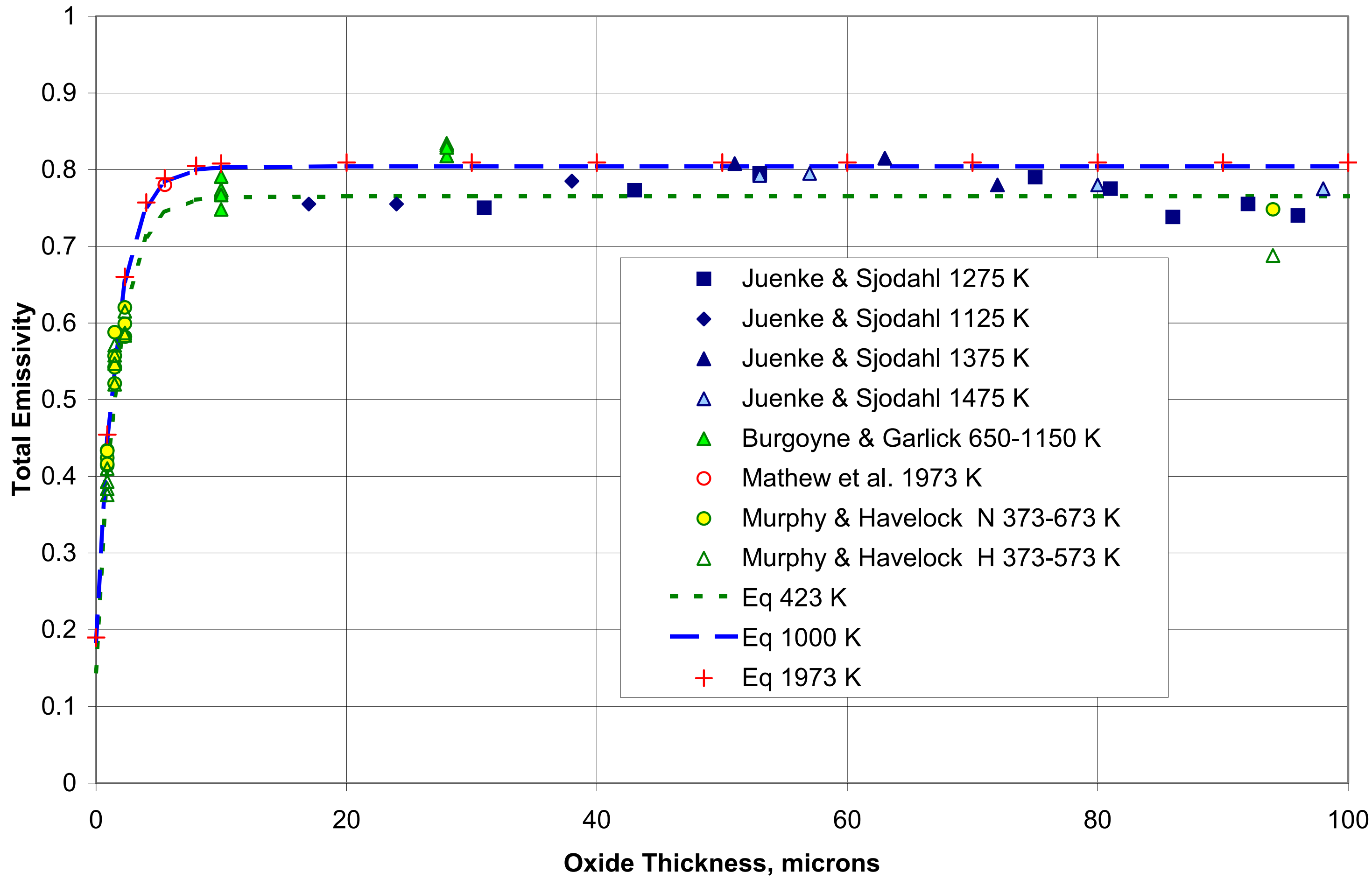

Fig. 8 Zircaloy Emissivity as a Function of Oxide Thickness

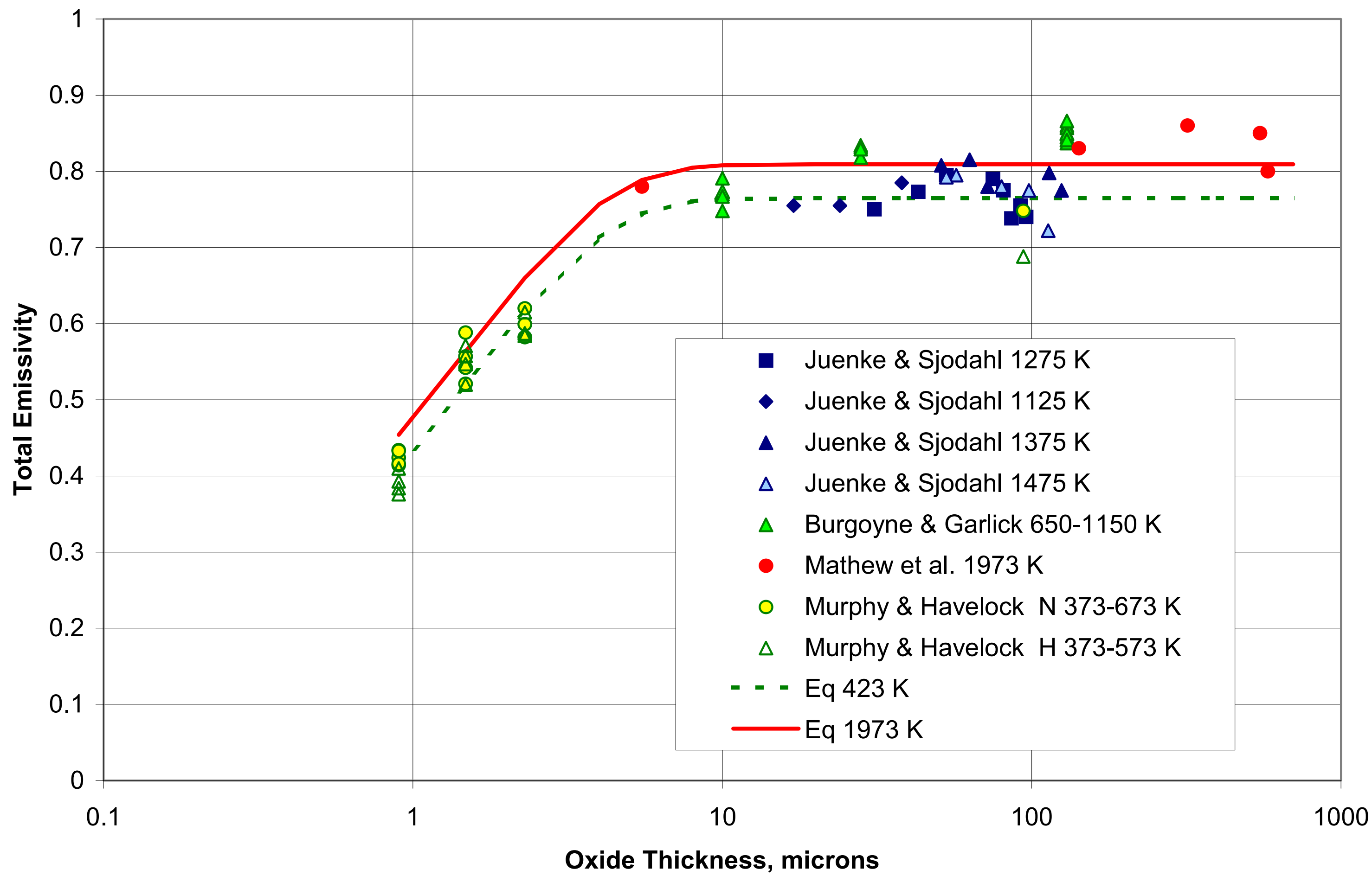

Fig. 9 Zircaloy Emissivity as a Function of Oxide Thickness

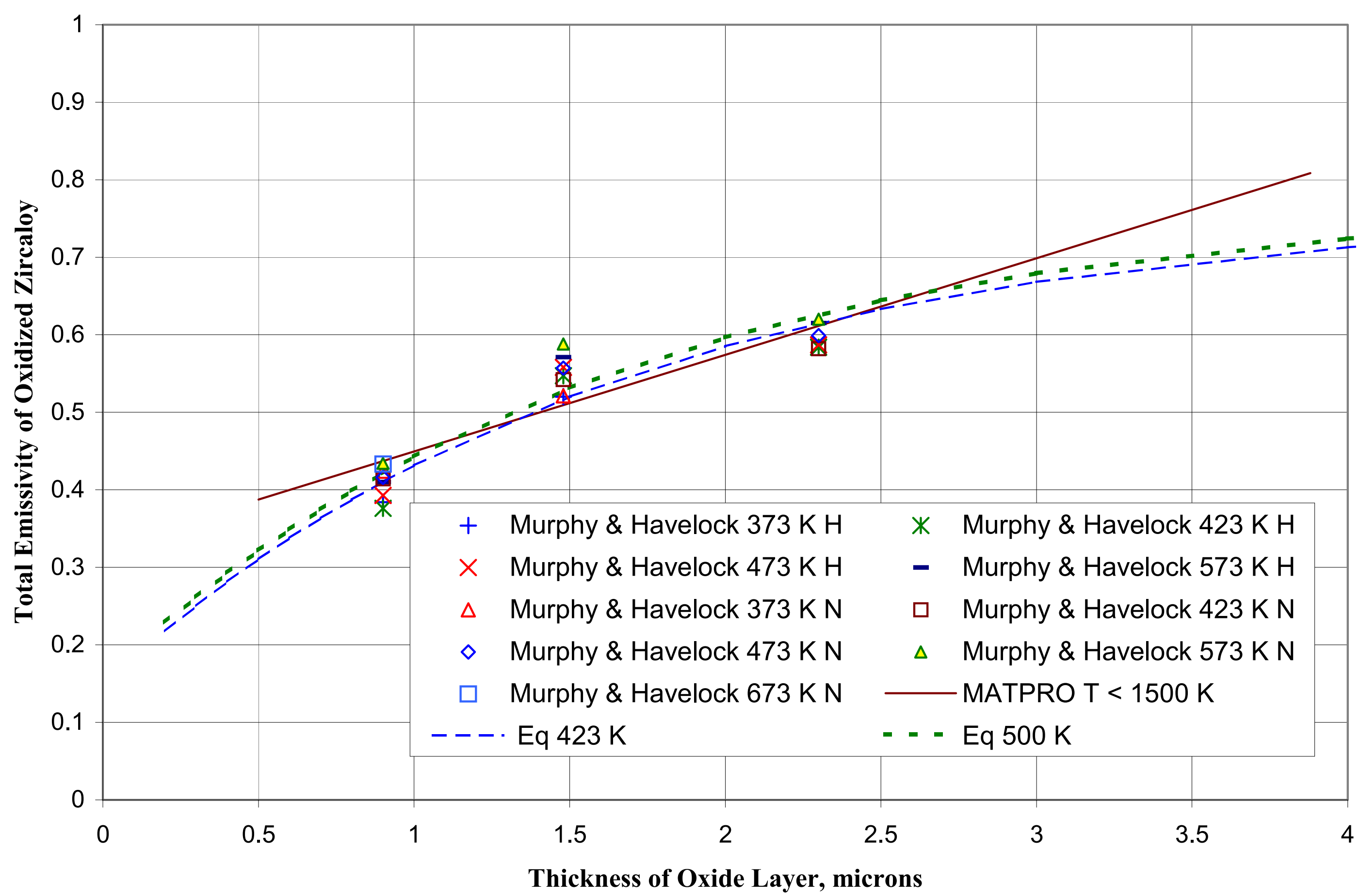

Fig. 10 Comparison of Murphy & Havelock Data with Eq.(2) and MATPRO

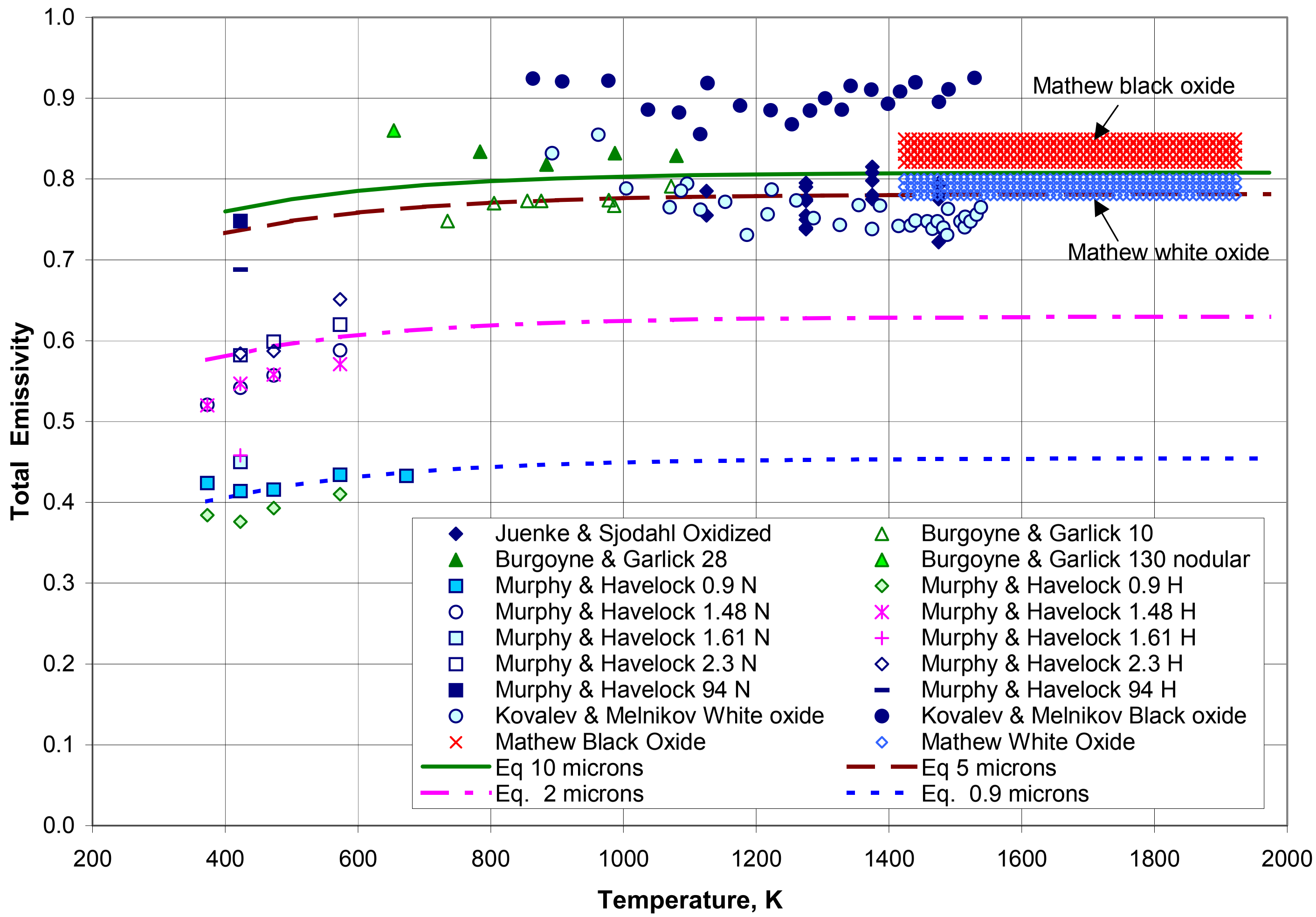

Fig. 11 Total Emissivity of Oxidized Zircaloy as a Function of Temperature