Zircaloy-4 (O) Solidus Temperatures

Preliminary Recommendation

The preliminary recommended equations for the solidus of Zircaloy-4 (O) are based on the recent measurements by Hayward and George [1]. The curve given by Howard and George to represent their data was read from their graph and fit by the following equations in which X stands for the oxygen content in atom percent.

For $0 \leq X \leq 11.01$at%,

$$T_S(K) = 2025.33 + 15.1043X + 0.0930X^2; \quad (1)$$

For 11.01 at% $\leq X \leq$ 15.5 at%,

$$T_S(K) = 2203; \quad (2)$$

For 15.5 at% $\leq X \leq$ 21.3 at%,

$$T_S(K) = 175.48 + 207.987X - 4.979X^2; \quad (3)$$

For 20.0 at% $\leq X \leq$ 22.5 at%,

$$T_S(K) = 2348; \quad (4)$$

For 22.5 at% $\leq X \leq$ 29 at%,

$$T_S(K) = 2222.248 + 13.506X - 0.35188X^2; \quad (5)$$

For $X >$ 29 at%,

$$T_S(K) = 2318; \quad (6)$$

The large number of significant figures in equations (1), (3), and (5) arise from the constraint of continuity at the endpoints. The data obtained by Hayward and George [1] and the curve produced by the above equations, which reproduces the curve presented by Hayward and George [1] are shown in Figure 1. Tabulated values of the solidus temperature for Zircaloy-4 (O) as a function of oxygen are given in Table 1 and

compared with the data of Hayward and George. Hayward and George give an uncertainty of $\pm$ 20 K for their data, which has been included as error bars in Figure 1.

Uncertainty

The estimated uncertainty in the recommended values is that given by Hayward and George for their data, $\pm$ 20 K, which is about 1%. Except for the 2301 K datum at an oxygen level of 17.1 atm%, the uncertainty in reproducing the curve and fitting the data is much smaller than the quoted uncertainty in the data. The uncertainty for this datum is 1.01%.

Discussion

Hayward and George compared their data with Zr-O solidus data of Ackermann et al. [2] and with values from MATPRO [3]. This comparison is shown in Figure 2. The MATPRO equations for the Zircaloy-O solidus temperature, T_{sol}, in K as a function of atom fraction of oxygen, y, are:

For $y \leq 0.1$

$$T_{sol} = 2098 + 1150y; \tag{7}$$

For $0.1 < y \leq 0.18$

$$T_{sol} = 2213; \tag{8}$$

For $0.18 < y \leq 0.29$

$$T_{sol} = 13389.5317 + 7640.0748y - 17029.172y^2; \tag{9}$$

For $0.29 < y \leq 0.63$

$$T_{sol} = 2173; \tag{10}$$

For $0.63 < y \leq 0.667$

$$T_{sol} = -11573.454 + 21818.181y; \tag{11}$$

For $y > 0.667$

$$T_{sol} = -11572.454 + y(1.334 - y)21818.181; \tag{12}$$

Hayward and George found reasonable agreement between their Zircaloy-O and the Zr-O composition ranges of Ackermann et al.[2] for the various types of reactions (i.e.

peritectic, eutectic, congruent melting). They attributed the lower solidus temperatures at low oxygen content for Zircaloy-O compared to Zr-O to either influences of the Zircaloy alloy elements such as Sn or to possible pre-oxidation of Zr samples of Ackermann et al. during heating in high density ZrO_2. From comparison of their data at high oxygen content with the solidus temperatures for O-saturated Zircaloy given in MATPRO, they concluded that the values quoted in MATPRO are probably low by 145-185 K and recommended a value of 2318 $\pm$ 20 K be used for the solidus temperature of O-saturated cladding in future model revisions.

The recommended equations were obtained by least squares fits of the curve given by Hayward and George constrained for continuity at the endpoints of each equation. In Table 1, values calculated with the recommended equations are compared with the data tabulated by Hayward and George. These equations fit the data of Hayward and George with an error of less than 1% except for the datum 2301 K at 17.1 atm% O, which is fit within 1.01%, or 24 K. Hayward and George estimate the experimental uncertainty of their data as $\pm$ 20K. Thus except for this one datum, which is higher than the recommended equation by 24K, all the values given by the recommended equations are within the experimental uncertainty given by Hayward and George.

Figure 3 shows the data of Hayward and George, the recommended equations, Eq.(1) – Eq.(6), the data of Ackermann et al., and the equations given in MATPRO. The MATPRO equations are about 4% higher than the data of Hayward and George at low oxygen levels (less than 10 atm%) and are within 1% of the data at oxygen levels from 10 to 15 atm%. Above 15 atm% oxygen, the MATPRO equations are low relative to the data of Hayward and George by 4% to 6% with the deviation increasing as the oxygen level approaches saturation. Hayward and George state that at saturation, the MATPRO recommendation is low by 145 K to 185 K or by 6 to 8%. Therefore the equations based on the curve of Hayward and George are recommended in place of the equations given in MATPRO.

Table 1. Comparison of Recommended Equations with Data of Hayward & George

Oxygen, atm%	Solidus Temperature, K	
	Data	Recommended
0.74	2037	2037
2.3	2070	2061
3.7	2072	2082
5.5	2112	2111
8.3	2153	2157
8.7	2169	2164
9.1	2151	2170
9.9	2188	2184
10.2	2207	2189
10.4	2195	2192
11.2	2188	2203
15.5	2207	2203
17.1	2301	2277
21.0	2327	2347
21.3	2358	2348
25.7	2328	2337
26.9	2337	2331
29.2	2321	2318
32.5	2318	2318
34.4	2318	2318

References

1. P. J. Hayward and I. M. George, *Determination of the solidus temperatures of Zircaloy-4/oxygen alloys*, J. Nucl. Mat. **273**, 294-301 (1999).
2. R. J. Ackermann, S. P. Garg, and E. G. Rauh, J. Am. Ceram. Soc. **60**, 341 (1977).
3. D. T. Hagrman, Ed., "SCDAP/RELAP5/MOD 3.1 Code Manual:MATPRO – A Librarty of Materials Proeprties for Light-Water-Reactor Accident Analysis, **NUREG/CR-6150, EGG-2720 Vol.4** (1995).

Fig. 1 Recommended Equations for Zircaloy-4(O) Solidus Temperature

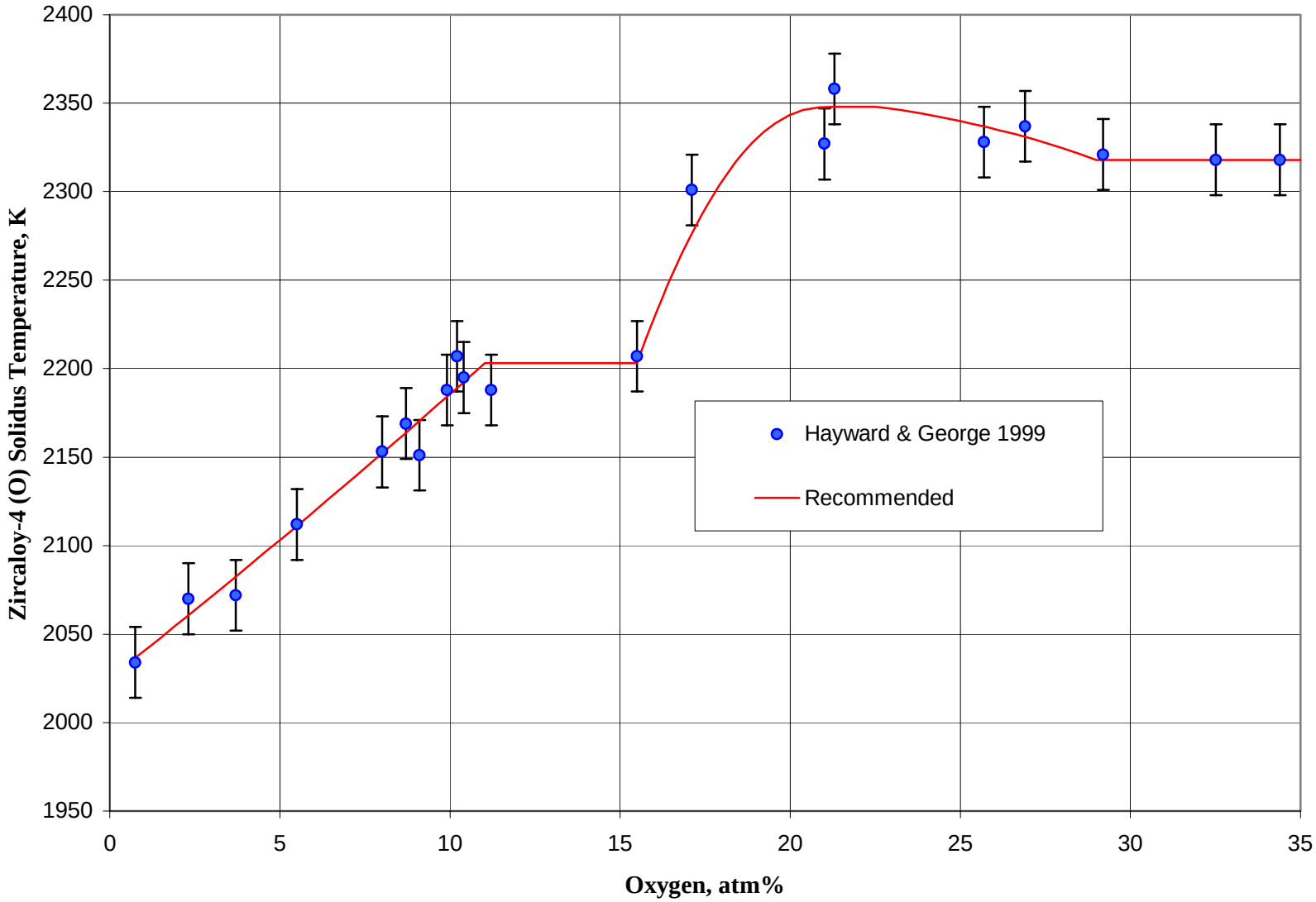

Fig. 2 Comparison of Zircaloy- 4 (O) Solidus Temperature Data with MATPRO

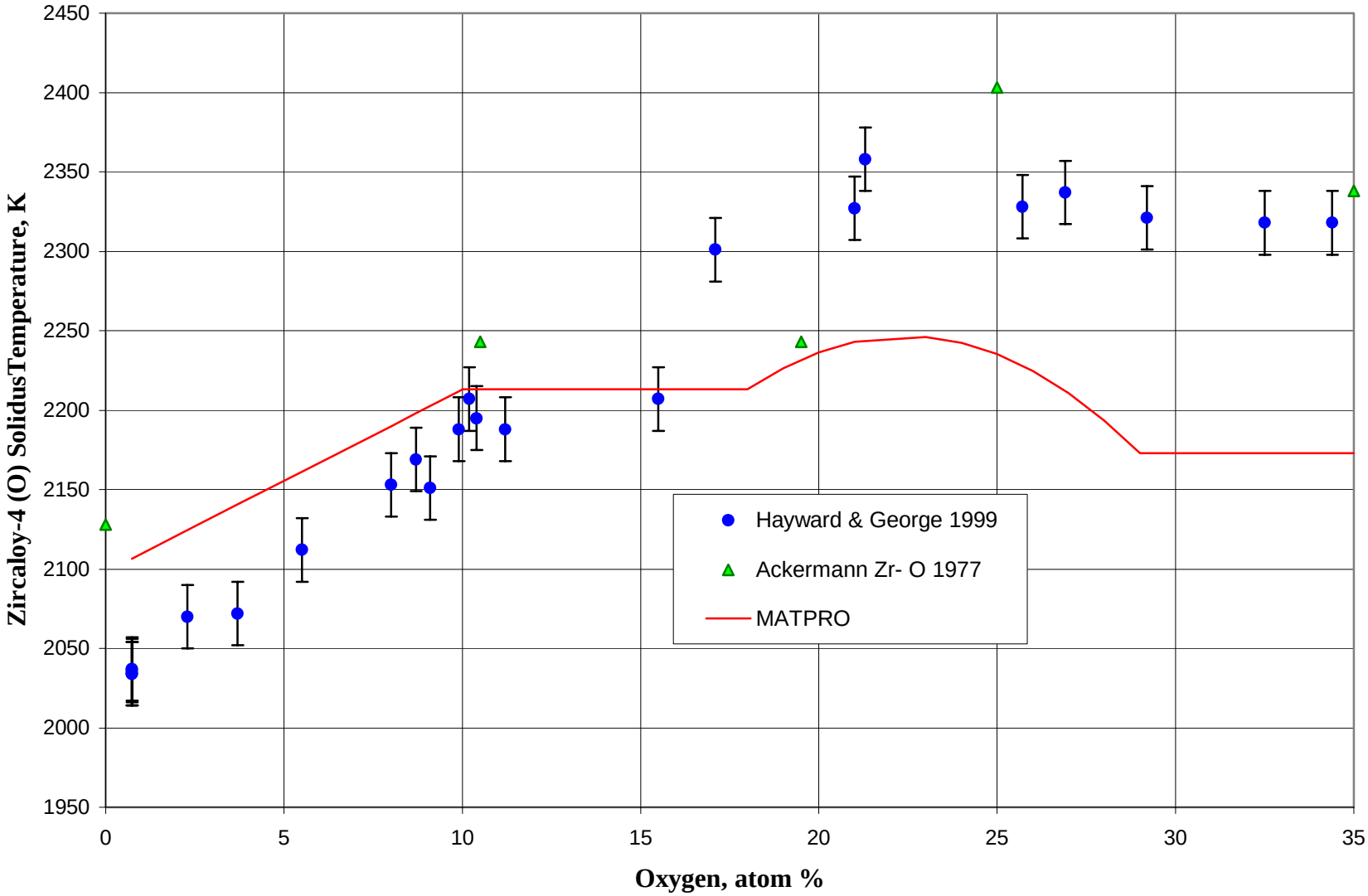

Fig. 3 Comparison of Recommended Equation with MATPRO and Data