

An oxidation mechanism map for tungsten

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Abstract

A tungsten oxidation mechanism map is developed to clarify literature confusion about the dominant oxidation kinetic regime and to enable improved predictions in extreme environments. Thermogravimetry data is systematically extracted from 14 papers in the range 600–1600 °C and treated as three distinct kinetic regimes: parabolic oxidation, linear oxidation, and sublimation. A mechanism map is constructed that shows thickness contours for each regime in time-temperature space. The map enables consideration of a fusion reactor accident combining loss of coolant and vacuum, in which a tungsten first wall could reach ~1200 °C for several weeks. Complete oxidation of the first wall and 2 mm of sublimation is predicted. Similar maps must be developed for accident tolerant tungsten alloys if reliable predictions are to be made about their performance.

Keywords

Tungsten, oxidation kinetics, fusion reactor, accident tolerance, sublimation

Tungsten is a leading candidate material for fusion engineering applications due to its high melting temperature, thermal conductivity [1]–[3], and sputtering resistance [4]. Although challenges remain in achieving adequate mechanical properties [1], [5]–[8], tungsten has been proposed as the first wall and divertor of the International Thermonuclear Experimental Reactor (ITER). In ITER the radiation damage and neutron flux will be moderate [6], [9]–[14].

However, in a demonstration power plant reactor, e.g. DEMO, such neutron fluxes will be significantly higher, leading to extensive radioactive product formation (Re, Os, Ta, and Hf) [6],[15], [16]. These products must be contained, particularly as Os is toxic. Their release could occur in a loss-of-vacuum accident (LOVA) when air could ingress into the vacuum vessel, causing oxidation of the plasma-facing surface. If combined with a loss-of-coolant accident (LOCA), the temperature could rise further still due to continued radioactive decay, potentially reaching 1200 °C and remaining at that temperature for several weeks [17]. This would oxidise and subsequently sublimate significant amounts of material into the environment [6], [10].

The oxidation of tungsten is well documented [1], [18]. Despite its high melting point, it oxidises readily, and powders are pyrophoric if <0.2mm [19]. The oxide scale is dominated by porous WO₃ in the range 0–1200°C [20]. Fine interlayers of a denser WO₂ phase form at the metal-oxide interface in a transitory manner, with the interlayer being subsequently converted to WO₃ as the scale thickens [20], [21].

Generally, there are three kinetic growth laws reported, which occur sequentially during an oxidation experiment. The first is the logarithmic, or initial transient [1], [22]–[24]. This process terminates when the thickness of the oxide reaches ~50 Å [22], therefore it will not be considered further as its role in accident-relevant scales (mm-thick), is negligible. The next stage follows a parabolic rate law, describing protective oxide film formation. Parabolic behaviour is reported in the

range 400-1000 °C [25]–[27]. The rate is limited by oxygen vacancy diffusion within the scale, and is therefore dependent the scale stoichiometry and structure.

Once the scale exceeds a critical thickness, it cracks on the macroscale [20], [28], [29]. Cracking is driven by compressive stresses due to the scale's lower density vs. the metal (by a factor of ~3.3 in the case of WO₃) [30]. Cracking often initiates at edges or protrusions due to stress concentrations [26], [31]. When cracking occurs, the diffusion barrier protection is lost, and the oxidation kinetics become linear [32]. The transition from parabolic to linear has been widely reported [20], [21], [33]–[35], however the transition parameters (e.g. time or scale thicknesses) are rarely quantified [36].

Equally important from an accident perspective is the subsequent sublimation of the scale. Sublimation follows linear kinetics [20], since it is limited by the exposed oxide surface area, which is generally constant. The picture is further complicated by experimental variables. E.g., the sample size [20], [21], [25], [34] and surface roughness [20], [31], [34] can affect reported rates of oxidation and sublimation. They also vary depending on the crystallographic orientation [20],[37], [38] and grain size [21], [31] of the material; and on the flow rate [39], the partial pressure [40], [41] and the moisture content [29], [42], [43] of the purge gas.

The above factors mean that reports of oxidation kinetic rate data have been inconsistent. This, combined with a lack of quantitative treatment of transition between kinetic regimes, means a robust quantitative understanding is still lacking. In this paper, inconsistent reports are unified by reanalysing the oxidation rate data in terms of distinct kinetic regimes. This permits the dominant kinetic processes to be quantitatively mapped as a function of time and temperature.

Data was extracted from literature thermogravimetry plots using the “Digitize Image” function of Origin. This method can achieve high levels of validity and reliability, with Pearson’s correlation coefficients of 0.993-0.998 when comparing measured and extracted datasets [44]. Where literature plots were fitted with a line, the data used was extracted from that line. While this method generates more data than was collected by the original authors, the advantage was reduced human error resulting from mis-identifying individual data points. **Table 1** summarises the oxidation rate studies that were assessed. Data from each study was fitted with a function of the form:

$$\frac{\Delta m}{A} = k * t^n, \quad (1)$$

where the exponent, n , can describe linear kinetics ($n=1$), parabolic kinetics ($n=0.5$), or some intermediate value ($n=0.5-1$). The transition from the parabolic to the linear regime was quantified by first visually identifying an approximate transition point. Second, **Eq. 1** was fitted to data either side of the initial transition by varying n and k , whilst excluding the data within the transition’s immediate vicinity (33% for the linear region and 50% for the parabolic region). In the parabolic region, the first 5-10 data points of each measurement were also excluded due to the initial logarithmic transient. At high temperatures (800 -1000 °C), deviation from the linear rate commonly occurred at the end of the measurements. This portion was excluded due to it likely being cause by recession of sample area and/or partial oxide sublimation. Finally, the fitted parabolic ($n\sim 0.5$) and linear ($n\sim 1$) lines were extrapolated, and their intersection was determined.

Table 1

Summary of oxidation literature, with the experimental conditions for each study. For oxygen partial pressure, the mixing gas is indicated in brackets.

Author	Reported kinetics	Temperature range (°C)	Time (h)	Oxygen partial pressure (atm)
Robyn [26]	parabolic	300-525	0.2-1.5	1
Gulbransen et al [25]	parabolic	400-500	2	0.1
Gulbransen et al [34]	parabolic	500-600	6	0.1
Gulbransen et al [34]	parabolic	600-1000	0.2-6	0.1
Dunn [27]	parabolic	700-1000	3	0.21 (air)
Wendel [20]	parabolic	500-800	2	5x10 ⁻⁶

Wendel [20]	parabolic	500-1000	2	5×10^{-6} (He)
Cifuentes et al [45]	parabolic	600	100	0.21 (air)
Louro et al [46]	parabolic	600-800	0.5	0.21 (air)
Cifuentes et al [36]	linear	600-800	100	0.21 (N)
Blackburn et al [41]	linear	800-1000	0.5	0.21 (Ar)
Baur et al [47]	linear	600-850	3	1.36-34
Cifuentes et al [45]	linear	700-800	100-20	0.21 (air)
Monge et al [35]	mixed	600	100	0.21 (air)
Wendel [20]	mixed	700-1000	2	5×10^{-6} (He)
Webb et al [48]	mixed	700-1000	0.5-3.3	1
Jepson et al [21]	mixed	500-600	2.5	0.1
Jepson et al [21]	mixed	800	30	1

Examples of the transition point determination are shown in **Fig. 1(a)**. Data are taken from Ref. [34] at 625, 700 and 900 °C. The time and mass gain of the transition, labelled t_{tr} and m_{tr} respectively, increase with increasing temperature. This intersection method was used on all graphs where a parabolic to linear transition was detectable.

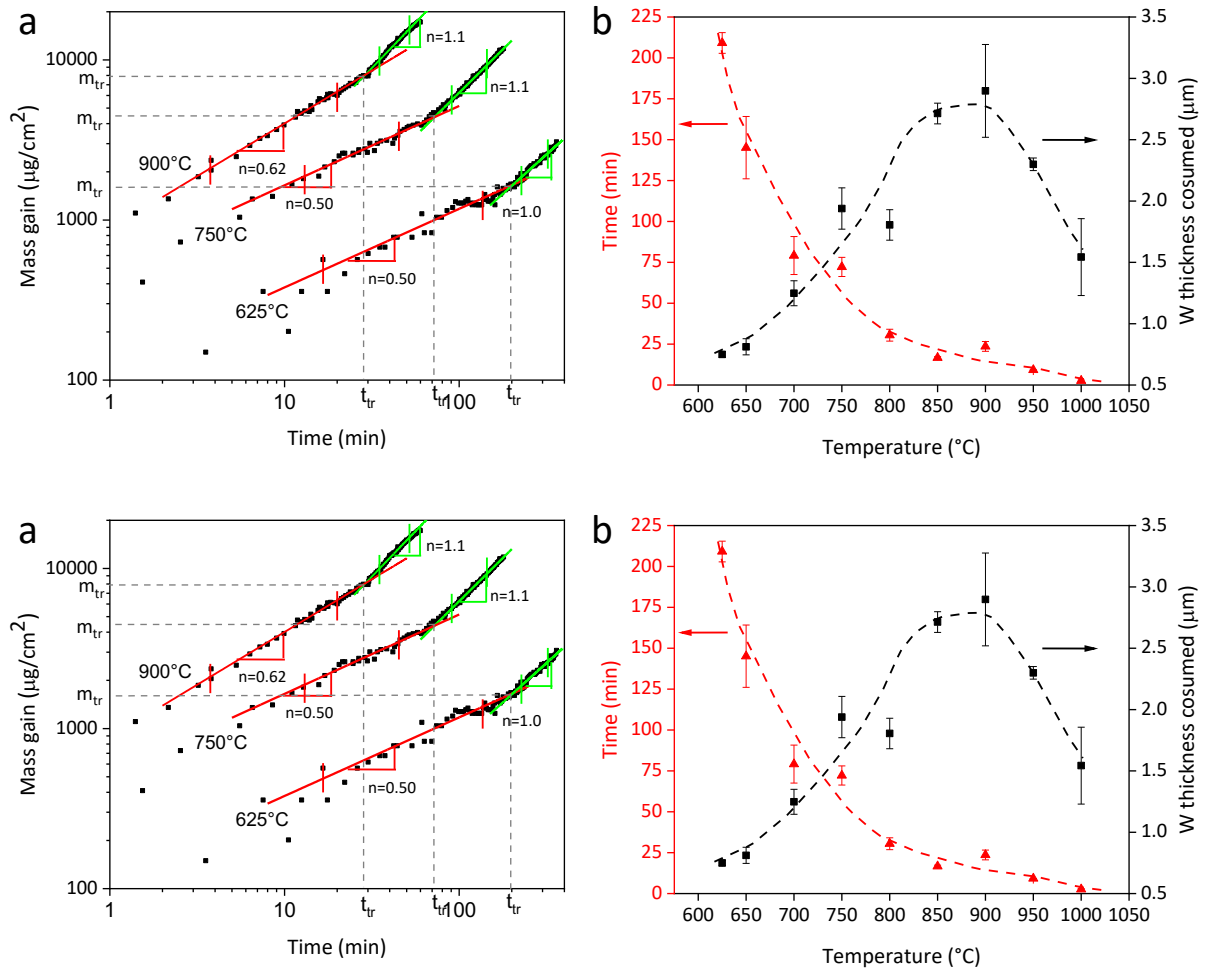


Fig. 1. Example of oxidation kinetic analysis from Ref. [34]. (a) mass gain data at 625-900 °C, showing the intersection method used to determine the transition points (m_{tr} and t_{tr}) from parabolic (red) to linear (green) kinetics. The included regions for fitting are marked with the vertical lines. (b) The kinetic transition time (red triangles, primary y-axis) and **corresponding W thickness consumed** (black squares, secondary y-axis) as a function of temperature. Error bars represent deviation between two fitting methods; one where all data points are included, and a second where only the outer 50% of data (i.e. furthest from the transition point) are included.

Fig. 1(b) quantifies the transition from parabolic to linear oxidation regimes. The respective exponents for each regime were in the range $n=0.4-0.6$ and $n=0.8-1.1$. The transition time (primary y-

axis) decreases monotonically with temperature. This can be explained by the exponentially increasing parabolic kinetic growth rate, meaning less time is required to grow a sufficiently thick scale such that the associated stress causes fracture. There was no apparent transition below 600 °C for the full experiment duration (360 mins) with corresponding kinetic exponents of $n=0.6-0.67$.

By contrast, the trend in the transition **thickness for W consumption** (secondary y-axis) was not monotonic. It is perhaps more meaningful than the time as it can be interpreted independently of growth rate. **The W thickness consumed was quantified as follows: First, the mass gain was converted into an equivalent mass of tungsten using the ratio of molar masses of W and WO₃ (or W and WO₂ for parabolic oxidation). These are 183.8, 231.8 and 215.8 g.mol⁻¹ respectively. Second, this mass was converted into a thickness using the density of pure tungsten (19.3 g/cm³). In Fig. 1(b), two regimes of behaviour are apparent: in the low temperature regime (600-900°C) the thickness increases with temperature, from approximately 0.8 to 2.9 µm. This suggests that the scale is becoming more resilient to fracture. The Tamman temperature of WO₃ ($T/T_m=0.5$) is 600 °C, above which thermally activated creep-like deformation mechanisms generally begin to occur, which could allow the oxide layer to partially-relieve thermal mis-match stresses, thus enabling a greater scale thickness before fracture. It is also possible that higher temperatures could cause a reduction in scale porosity due to sintering. In the second regime (>900 °C) the transition thickness begins to decrease progressively with increasing temperature. Further work is required to understand the physical origins of this decrease.**

Having quantified these transitions, we now assess the oxidation rate constants. In doing this, the data either side of the transition in graphs such as Fig. 1(a) are refitted with the theoretical values of n , i.e. 0.5 and 1. This makes the resulting rate constants less dependent on data extremities, which improves study-to-study consistency.

The resulting oxidation kinetic constants are shown in **Fig. 2**. Part (a) contains all the linear rate constants, k_l . The data are contained within 3 bands of oxygen partial pressure, low (0.1 atm, black), medium (0.2 atm, red), and high (3.4-13.6 atm, blue). The apparent activation energies were 118, 135, and 187 kJ/mol, respectively. k_l increases with oxygen partial pressure, as expected. The low and medium pressure energies are close that reported in Ref. [34] of 136 kJ/mol in the range 750-1000 °C, where linear growth was dominant. We therefore interpret this as being the activation energy for the surface $W+1.5O_2 \rightarrow WO_3$ surface reaction. NB: the high partial pressure data of Baur et al [47] was not collected with kinetic regime separation, and this may be the cause of its higher apparent activation energy.

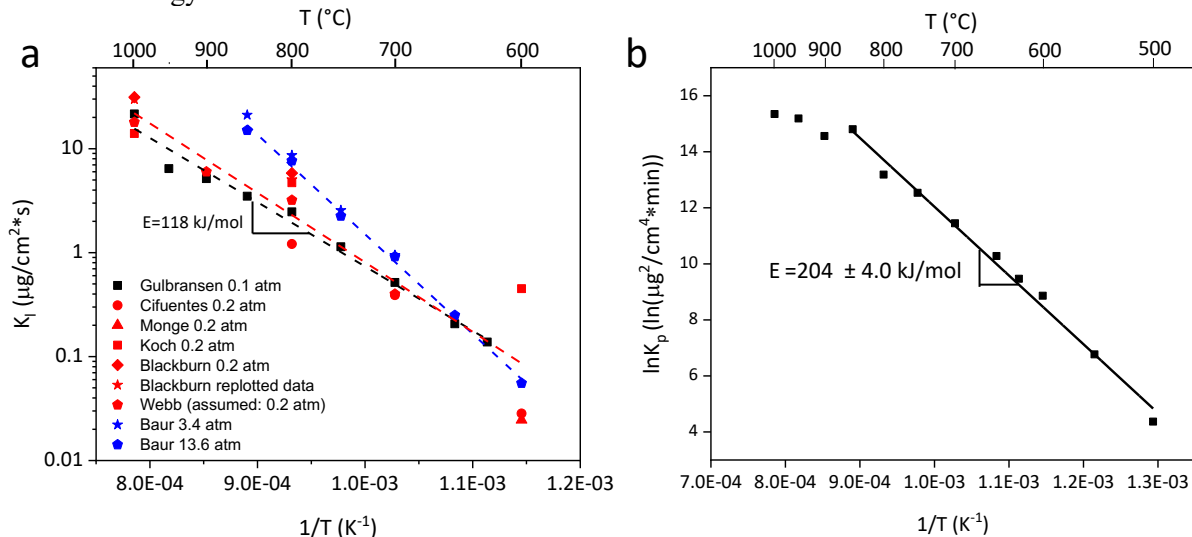


Fig. 2. Oxidation rate constants. (a) Linear rate constants, k_l , from Refs. [34], [35], [41], [47]–[49]. NB: data for Koch et al [49] are reported directly as the parabolic regime was already separated; data from Baur et al [47] are reported directly without any separation. (b) Parabolic rate constants, k_p , from Ref. [34]. **The solid line represents a line of best fit to the data below 850 °C**

Fig. 2(b) shows the parabolic kinetic constants extracted from Ref. [34]. The line of best fit is made for the data below 850 °C, since the data above this temperature levels off, presumably due to

the same effect causing the decrease in transition thickness in **Fig. 1(b)**. The resulting activation energy is 204 ± 4 kJ/mol. We interpret this as being the activation energy for diffusion of oxygen vacancies through WO_3 .

The two activation energies reported in **Fig. 2** straddle either side of previously reported activation energies, calculated without separating the two kinetic regimes. For example, Sika et al. reported 125 kJ/mol in the temperature range 568-908 °C, the partial pressure of oxygen was 0.05 atm [50], and Wendel reported 142-153 kJ/mol in the temperature range 500-1000 °C, at an O_2 partial pressure of 5×10^{-6} atm, depending on the polishing treatment [20].

The focus is now turned to sublimation. **Table 2** summarises the studies that were assessed. The temperature range analysed was higher (generally >1100 °C) to ensure the samples had been fully oxidised, and therefore the sublimation rate data was not significantly affected by simultaneous oxidation.

A typical sublimation data set taken from wire samples in Ref. [34] is shown in **Fig. 3(a)**. At 1100-1150 °C the sample initially gains mass, but after a few minutes the sample is fully oxidised and subsequently begins to lose mass due to sublimation. In the case of the 1200 °C sample, the oxidation completes very rapidly, thus the mass change signal decreases monotonically. The sublimation rates were calculated from the middle third of the sublimation-dominated regime, i.e. excluding the outer data extremities, to ensure the rate was not affected by simultaneous oxidation, or by excessive reduction of sample area.

Table 2

Summary of Sublimation literature, with the experimental conditions for each study.

Author	Temperature range (°C)	Time (min)	Pressure (atm)	Atmosphere
Klein [51]	1000	60	1	20% O_2 80% Ar
Blackburn [41]	800-1450		0-1	20% O_2 80%
Speiser [52]	1100-1400		1	Dry air
Gulbransen [34]	1100-1200	5-65	0.1	O_2
Stroke [10]	1200		1	Air

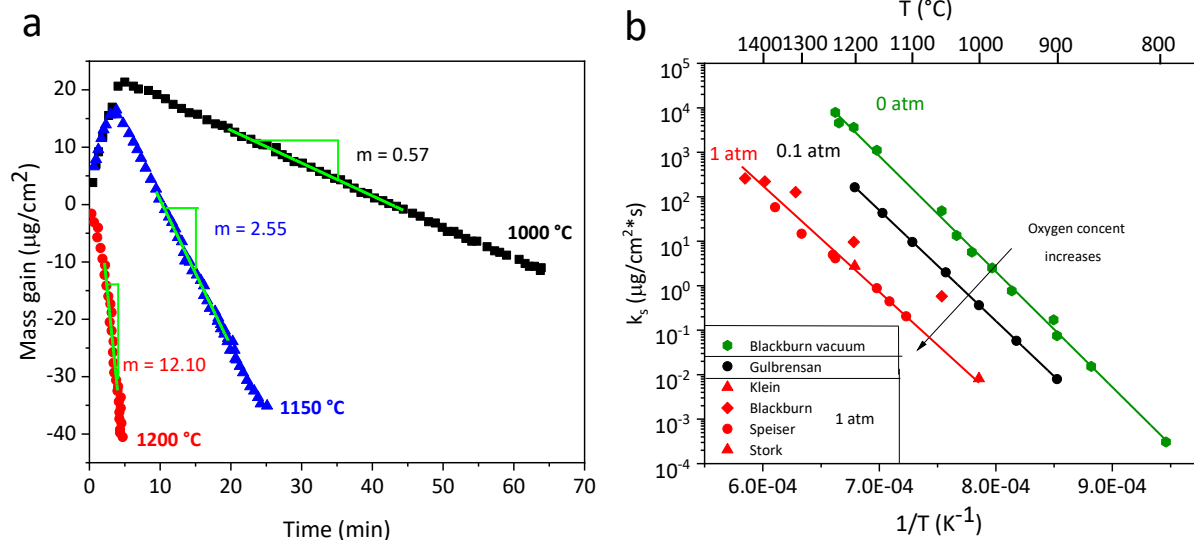


Fig. 3. Sublimation analysis. (a) Typical sublimation rate data at 1100-1200 °C. Sublimation rates were taken from the middle linear section of the negative slope. (b) Sublimation rate constants as a function of temperature and pressure. Data for Klein [51] & Gulbransen [34] are extracted from raw TGA data, e.g. Fig. 2.; data from Stork [10], Blackburn [34] & Speiser [52] are reported directly. The apparent activation energies are 497, 476, and 402 kJ/mol for 0, 0.1, and 1 atm respectively.

Fig. 3(b) shows the extracted sublimation rates, k_s , at various gas pressures of 0 atm (green), 0.1 atm (black) and 1 atm (red). The rates increase with decreasing gas pressure, e.g., by ~ 3 orders of

magnitude faster at 0 atm vs. 1 atm. The 1 atm pressure data from 4 different authors is generally in good agreement. However the data for Blackburn et al [41] was generally higher, which may be due to fluctuations in the sample temperature due to inconsistent furnace positioning, as stated by the authors.

Having quantified both the sublimation and oxidation kinetics, we can now compare them. **Fig. 4** shows both rates plotted at 1 atm of gas pressure, of which 0.2 atm is oxygen. These conditions are selected to represent realistic accident (i.e. atmospheric) conditions. The lines of best fit intersect at 1399 °C, which is taken to be the temperature at which the sublimation and linear oxidation rates are equal. NB: this is significantly higher than previous estimates. E.g., Blackburn et al reported 1350 °C [41], which can be explained by the anomalously high sublimation rates they reported. Gulbransen et al. reported 1220 °C [34], although this experiment was under a reduced gas pressure of 0.1 atm, which would dramatically increase the sublimation rates – by a factor of 10 or so according to **Fig. 3(b)** – with minimal change in the oxidation rate.

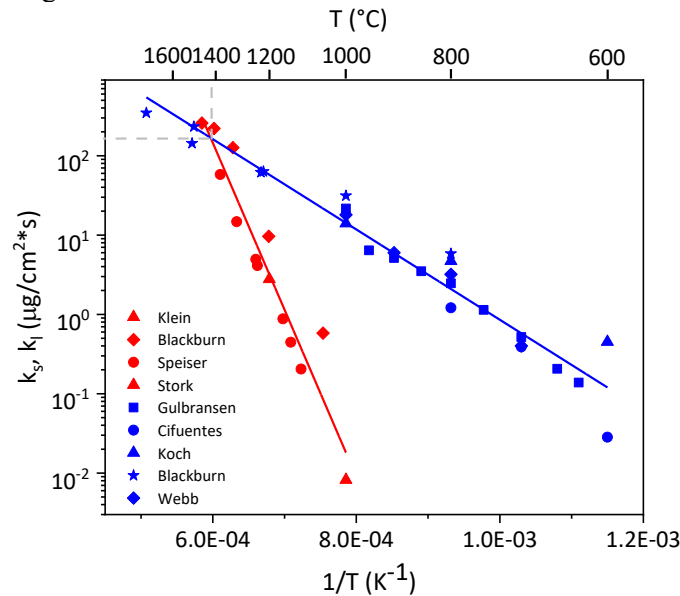


Fig. 4. Comparing sublimation rates, k_s , (red) with linear oxidation rates, k_l , (blue) at atmospheric conditions of 1 atm gas pressure and 0.2 atm O_2 partial pressure.

Table 3 summarises the rate equations developed from the fits in **Fig. 2** & **Fig. 3** that pertain to atmospheric conditions. **These mass gain equations can be converted into equations for W thickness consumed, using the same procedure outlined in Fig. 1(b).** Using these equations, thickness contours can then be plotted as a function of time and temperature to form a mechanism map, as shown in **Fig. 5**.

Table 3

Rate constants that constitute the rate equations of the form $k=k_0\exp(-E/kT)$.

Regime	k_0 ($\mu\text{g}/\text{cm}^2.\text{s}$)	E (kJ/mol)
Oxidation, linear	6.17×10^2	118
Oxidation, parabolic	$1.35 \times 10^{13*}$	204
Sublimation data	4.85×10^7	402

*Units for parabolic regime are expressed as $\mu\text{g}^2/\text{cm}^4.\text{s}$

Fig. 5 shows each of the three kinetic regions: linear (green), parabolic (red) and sublimation (blue). Thickness contours for each mechanistic regime are indicated in solid lines coloured accordingly. The parabolic-linear intersection points (squares) were taken from **Fig. 1(b)**. It is

interesting to note the dotted line of intersection does not pass perfectly through these points. This is likely because **Fig. 1(b)** was based only on data from Ref. [30], whereas the rate equations in the map are averaged from many different studies.

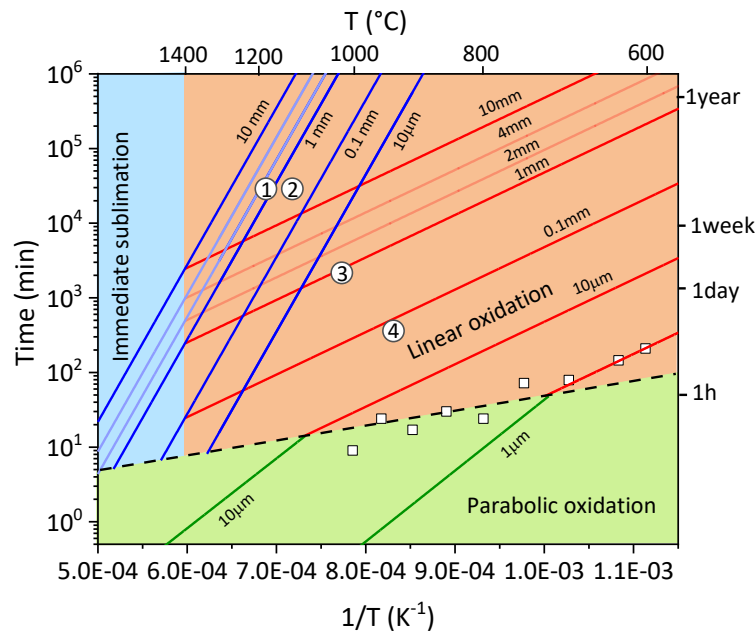


Fig. 5. Oxidation mechanism map in the temperature range of 600-1600 °C and up to 2 years. Contours indicate the thickness of the metal consumed. The parabolic, linear, and sublimation regions are shaded in green, red, and blue respectively. The numbered circles (1-4) indicate various accident scenarios predicted by Maissonier et al for different power plant models (models C, B, A, and D respectively in Table 1 of Ref. [17]).

The map allows several practical engineering considerations to be made. We consider the tungsten tiles in a DEMO reactor, suggested to be 2-4 mm [53], the thickness of which is shaded onto **Fig. 5**. Also considered is the thermal transient experienced in a LOCA, for various DEMO designs considered by Maissonier et al [17] (labelled 1-4). The worst-case design (1) falls far beyond the shaded red bands, indicating full oxidation of the tiles. It also lies on the lower edge of the shaded blue bands, indicating approximately 1-2 mm (i.e. about half) of the oxidised tile would be sublimated.

NB: this is a worst-case prediction, as in reality an overpressure of WO₃ gas may build up inside the reactor, leading to a decreased sublimation rate. The map also highlights a stark dependence on the reactor design, with points (3) and (4) yielding far less catastrophic consequences, however the worst-case scenario is clearly unacceptable.

The map may also have implications for the development of accident tolerant W alloys and coatings. While a parabolic to linear transition is not commonly reported for such alloys, the formed oxides densities are still relatively low compared to the allow substrate (e.g. Cr₂WO₆ is ~6.4g/cc, in the case of W-Cr-Y alloys [6]). Therefore, in principle, scale break up could occur once a critical thickness is reached. This is particularly true when the scale thickness approaches the thickness of the coating. It is therefore essential that such accident tolerant alloys and coatings are investigated at longer times and higher temperatures, and that oxidation mechanism maps are developed for these materials.

In summary, the available data for the kinetics of W oxidation and WO₃ sublimation have been re-evaluated. A repeatable transition from parabolic (protective) kinetics to linear (unprotective) kinetics is found. The transition time decreases logarithmically with increasing temperature. Above ~1000 °C sublimation processes become important, with its rate becoming equal to the oxidation rate at 1399 °C in air at atmospheric conditions.

By separating the oxidation data into parabolic, linear and sublimation regimes, three kinetic relationships were derived, with activation energies of 118, 204, and 402 kJ/mol respectively. The rate limiting processes are attributed to being (i) oxygen vacancy diffusion in WO₃, (ii) to $1.5\text{O}_2 + \text{W} \rightarrow \text{WO}_3$ surface reaction, and (iii) WO₃ vaporisation, respectively.

The above laws allowed a map to be constructed as a function of time and temperature, showing metal recession thickness contours for each mechanism. The map shows that 2-4mm DEMO reactor tile would be fully oxidised, and a substantial portion (~50%) could be sublimated under the harshest conditions modelled (20 days at 1180 °C).

The study reinforces the need for improved accident tolerant tungsten alloys and coatings, and suggests that in future work, oxidation mechanism maps are developed for these materials.

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