



## Regular Article

# Tungsten carbide is more oxidation resistant than tungsten when processed to full density



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## ABSTRACT

Previous studies report that WC oxidises in air more readily than W. However, systematic thermogravimetric studies reveal considerably slower oxidation kinetics in WC samples, which outperform previous measurements by 1–2 orders of magnitude. By combining X-ray diffraction and electron microscopy, the enhanced stability in WC is explained by a dense interlayer of sub-stoichiometric  $WO_3$ , approximately 10  $\mu\text{m}$  in thickness, which forms adjacent to the substrate/oxide interface. The faster oxidation kinetics from previous studies are explained by the comparatively low densities of samples used.

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Tungsten and its carbides have excellent high temperature properties such as strength, stiffness, and thermal conductivity. Combined with their relatively low cost, they are being developed for many technologies requiring extreme environments, such as nuclear fusion reactors. In particular, W is a leading candidate for structural and armour components [1], while WC shows promise for shielding in compact spherical reactors [2]. The drawback of these materials is their susceptibility to oxidation at relatively modest temperatures [3], which can present major safety issues; e.g. under accidental conditions in a nuclear fusion reactor, where oxidation could release tungsten oxide vapours and transmutation products [4].

The kinetics of tungsten oxidation have been reviewed extensively [5–7], and can generally be categorised by three temperature regimes: From about room temperature to 500 °C, a protective bluish oxide scale of substoichiometric  $WO_3$  forms, leading to parabolic oxidation kinetics [5,7–9]. Above about 500 °C, a yellow  $WO_3$  scale begins to grow, whilst retaining the protective blueish interior below [5,9]. The outer layer is generally highly cracked and thus unprotective [10,11], therefore linear kinetics are generally observed [5–7,12,11]. The parabolic-to-linear transition is time-dependent as cracking-onset is dependant on scale thickness [5]. Finally above 1000 °C, volatilisation of the  $WO_3$  scale becomes significant, eventually leading to overall mass loss of the sample [10].

The picture for pure WC is less clear, despite much work on composites such as WC–Co [13–16]. The oxidation kinetics of WC were reported to be faster than W – by about an order of magnitude – e.g. in the range

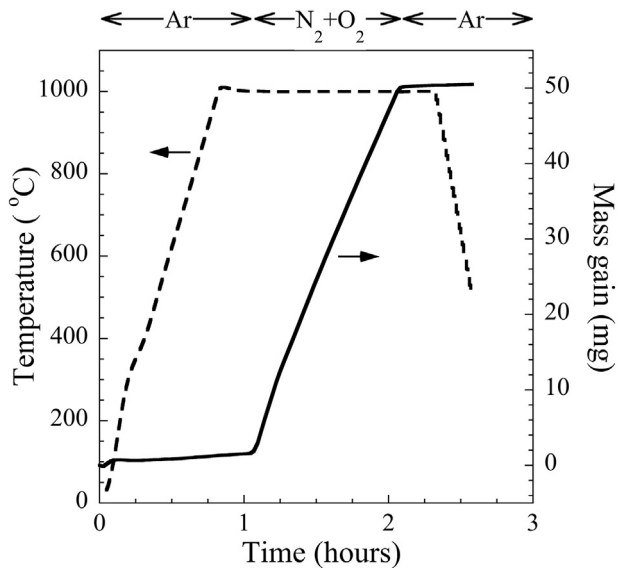
700–1000 °C [12] and 700–900 °C [17]. Poor carbide performance was explained by formation of  $CO_2$  gas at the interface [12], inducing excessive porosity and scale cracking. More recent evidence has cast doubt over these initial studies; at least in the range 0–500 °C, where thicker oxide scales were reported on W [18,19]. On a related contradiction, it is frequently cited that pure WC oxidises faster than WC–Co [17,20,21], but increasing Co content is generally found (although not always [16]) to increase the oxidation rate [13,15]. Thus, the literature is inconsistent, and what is more, no systematic comparison exists over a wide temperature range.

We report the oxidation kinetics of pure W and WC between 600 and 1000 °C. Counter to previous studies [12,17], we find the rate of oxidation in our WC samples is a factor of 10 or more slower. This discrepancy is explained by formation of a dense protective off-stoichiometric oxide interlayer in our samples, which would have been prevented from forming in previous studies where samples were highly porous.

Tungsten rod (Alpha Aesar, 99.7% purity), and tungsten carbide pellet (SPS Syntex, Ltd.), were cut into samples of about  $6 \times 3 \times 3$  mm, i.e. about 1 g each. For each oxidation experiment, samples were loaded into an alumina crucible inside a STA 449 F5 Jupiter Thermogravimetric Analyser (TGA). Fig. 1 shows the mass change and temperature profile during a typical experiment at 1000 °C. The sample was heated to the set-point in high purity argon, and held isothermally for 1 h. For lower temperatures, longer dwell times of about 2, 3, 10 and 15 h were used at 900, 800, 700 and 600 °C respectively. Once the temperature stabilised, synthetic air (80%  $N_2$ ; 20%  $O_2$ ) was flowed over the sample at 100 ml/min for the test duration, after which the flow gas was switched back to Ar and cooled. The mass gain signal in Fig. 1 shows a stable and repeatable increase, which initiates at the instant the air is flowed over the sample.

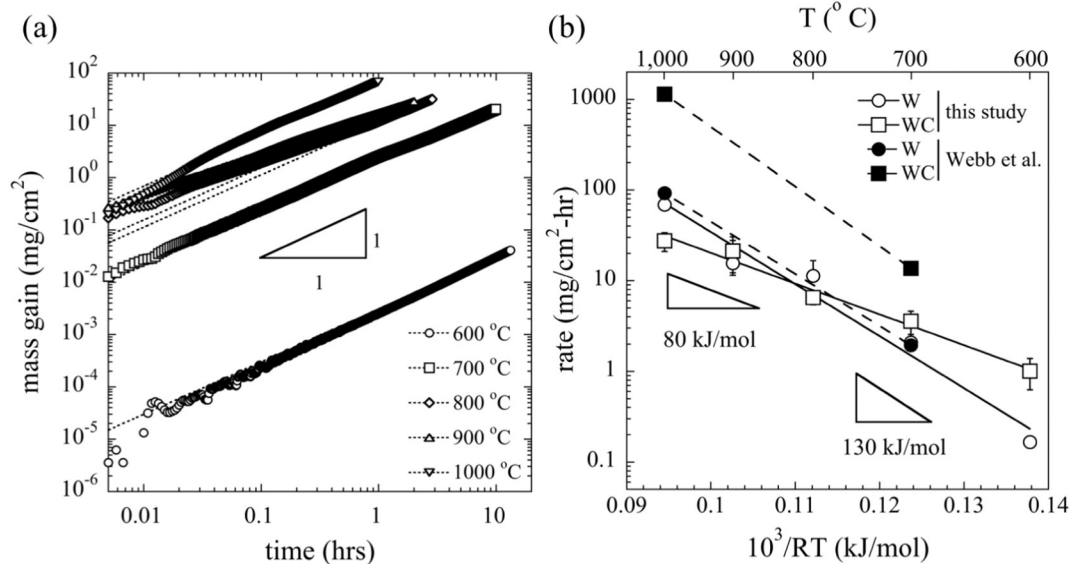
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**Fig. 1.** Overview of a typical TGA experiment, showing the temperature profile, and injection of synthetic air once the set-point is reached.

To relate the mass gain signal to a true oxidation rate, the instantaneous WC-substrate surface area must be known. The initial area of each specimen was calculated from its dimensions (as measured using a micrometre of accuracy  $\pm 0.002$  mm), from which the reduction in area of the sample was corrected for by assuming firstly that the WC substrate (of density  $15.5 \text{ g/cm}^3$ ) recedes isotropically in all directions, and secondly, that it is fully converted to  $\text{WO}_3$  (i.e.  $195.8 \rightarrow 231.8 \text{ g/mol}$ ), with carbon dioxide gas being released into the vapour phase. A similar calculation was performed for W. The resultant oxidation rates are plotted in Fig. 2(a) for pure W at various temperatures. The plot is on a log–log scale, and thus the gradient of the line reveals the nature of the kinetic trend. At all temperatures, the signals tend toward a gradient of  $m = 1$  at long times, which is indicative of linear oxidation kinetics, as is often reported for W in this temperature regime. The rate constant at each temperature, as calculated from the straight-line fit, is plotted as a function of inverse temperature in Fig. 2(b), alongside similar results for pure WC, where again linear kinetics are observed.



**Fig. 2.** Oxidation kinetics of W and WC. (a) shows linear oxidation kinetics for W. The rate constants are plotted (open circles) in (b) along with results for WC (open squares), as a function of inverse temperature, yielding activation energies of 130 and 80 kJ/mol respectively. Compared to the literature (closed symbols), our rate constants agree relatively well for W, however those for WC are dramatically lower. Error bars represent largest deviation in slope from fits to final or initial 10% of data.

The data can be fit with an Arrhenius-law, from which the apparent activation energy is lower for WC vs. W (80 and 130 kJ/mol respectively). Correspondingly, WC oxidises faster at low temperatures, but slower at high temperatures, with a cross-over occurring around 800–900 °C. The rate constants from Webb et al. [12] (which broadly agree with Kieffer and Kolbl [17]) are superimposed on the plot – as determined from linear fits to reported oxidation curves. Our methods are nominally the same, and as expected, our rate constants for W appear to agree. However there is stark disagreement for WC; our measured rates are about an order of magnitude lower.

To further elucidate the discrepancy between this study and the literature [12,17], the structural evolution in the WC oxide layer is now considered in detail. Fig. 3 depicts the change in the oxidised WC surfaces at increasing temperature: Part (a) shows a series of X-ray Diffraction (XRD) patterns from the oxidised WC surfaces, which were acquired on a Panalytical Pro instrument at a rate of  $2.5^\circ/\text{min}$ , and matched to ICDD Powder Diffraction Files (PDFs). A gradual structural transition is detected: (i) orthorhombic  $\text{WO}_3$  (PDF 20-1324) at 600 °C; (ii) triclinic  $\text{WO}_3$  (32-1395) at intermediate temperatures; and (iii) tetragonal  $\text{WO}_2$  (35-0791) at 1000 °C. Part (b) shows images of these oxide surfaces, taken on a JSM 6010 scanning electron microscope (SEM) in secondary electron (SE) mode. At low temperatures the scales are highly cracked, however, there was a general trend across all samples toward less cracking in the scale at higher temperatures; at 700 °C the cracks are spaced only about 50  $\mu\text{m}$  apart, at 800 °C they have perhaps a 200  $\mu\text{m}$  separation, and at 900 °C they are barely visible. The driving force for crack growth is likely the large ratio between the theoretical density of carbide and the oxide,  $\rho_{\text{carbide}}/\rho_{\text{oxide}} = 2.2$ , leading to compressive stresses in the plane of the pellet surface. The lack of cracking at high temperature suggests that the volume expansion can be accommodated by plastic deformation; at 1000 °C the oxide layer is at about  $0.73 T_m$ , i.e. above the threshold for diffusive creep processes in oxides – which typically begin in oxides on the order of  $0.7 T_m$  [22]. The lack of cracking in the outer scales at high temperatures suggests that some other short-circuit path, such as open porosity, must account for its unprotective nature.

To explain this structural transition, samples were sectioned normal to the surface by manual polishing to reveal the phases present below the surface. Between 600 °C and 800 °C the scales are homogeneously  $\text{WO}_3$  throughout, however at 900 °C and 1000 °C, sectioning revealed three different phases. Fig. 4 shows the structure at 1000 °C in detail,

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