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On the oxidation mechanism of pure tungsten in the temperature range 600–800 °C

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Abstract: The oxidation behavior of International Thermonuclear Experimental Reactor (ITER) reference tungsten grade has been evaluated in dry air in the temperature range 600–800 °C. At 600 °C, the scale remained protective while the integrity of W18O49 layer was kept. Rapid increase in mass gain resulted from massive cracking at local areas in the W18O49 layer. Then, a coarse non protective columnar WO3/2 scale was developed which favoured rapid inward oxygen transport into the alloy. At 700 and 800 °C, growth stresses in the scale were released through local cracking. At this stage, WO3/2 became progressively transformed into WO3 when the oxygen partial pressure increased across the scale thickness.

Keywords: C. High temperature corrosion, C. Oxidation, C. Kinetic parameters.

1. Introduction

Selection of the plasma facing materials (PFMs), i.e. the materials that will interact with the fusion plasma directly, is a critical issue for the success of the ITER and the development of future fusion power plants [1–4]. PFMs will operate under extreme conditions of temperature, irradiation and thermal stresses because of their direct exposure to the fusion plasma. Furthermore, material choice plays a central role in the environmental safety of fusion power reactors in future commercial energy plants [5,6]. A suitable PFM should contain elements of reduced activation in such a way that production of radioactive by products and tritium inventories are minimized [7]. These considerations as well as working conditions of plasma facing components (PFCs) reduce the availability of material candidates to those based on C, V, W, Ti and Be [8].

However, PFCs based on low Z materials have a short erosion lifetime due to their high sputtering yields under the plasma particles bombardment and radiation enhanced sublimation [9]. Furthermore, neutron irradiation increases tritium retention on beryllium and carbon base materials, rising safety hazards and reducing environmental attractiveness of fusion power plants due to accidental release of tritium and/or production of hazardous nuclear by products [7]. In addition, low melting point and high toxicity of beryllium have dissuaded about the use of this alloy in fusion reactors.

Properties such as very high melting point and very low vapor pressure, low sputtering yield, good thermal conductivity, low thermal expansion coefficient, high strength at high temperatures, low retention of tritium and good dimensional stability under neutron irradiation make tungsten, at present, the most promising candidate material for building divertor in PFCs at the ITER and future fusion reactors. Its major drawback, however, is the poor oxidation resistance which would cause irreversible detrimental effects on physical and chemical characteristics of W based components [3,10]. Even though the PFCs will operate in vacuum condition, forfuitous scenarios such as a LOCA event (Loss of Coolant Accident) or air ingress as a result of failure of the vessel’s integrity, can lead to oxidizing atmospheres which will have harmful impact on the operation of PFCs [11,12]. In case of emergency shutdown of a fusion power reactor, the temperature of tungsten PFCs would remain above 450 °C for several weeks [12]. An oxidizing atmosphere at these temperatures would enhance the oxidation rate through the formation of highly volatile radioactive tungsten oxides [13]. Thus, an assessment of the oxidation characteristics of ITER grade W appears to be necessary to update the database of tungsten for fusion applications [8].

Oxidation of tungsten produced by different routes and with different grade of purity has been widely studied in the past [14–22]. These studies have concluded that the oxidation kinetics of tungsten is quite complex. This complexity arises from the wide variety of oxides formed during oxidation as well as the development of stresses in the course of the oxidation. These two reasons seem to be the origin of the discrepancies regarding tungsten oxidation, as clearly manifested in the excellent review by Ivanov et al. [23].

In this work, the oxidation behavior of ITER reference tungsten grade has been studied in dry air in the temperature range 600–800 °C. This study tries to: (i) Get better understanding on the oxidation mechanism of tungsten through the analysis of the structure and nature of the oxides composing the scale. (ii) Provide useful oxidation data on ITER reference tungsten grade.
2. Experimental procedure

Oxidation tests at 600 and 700 °C were carried out on disks, 10 mm in diameter and 1 mm thick, cut from a rod of a swaged ITER reference tungsten grade (99.97% purity). Tests at 800 °C were done on coupons 5 × 5 × 2 mm³. All major surfaces were abraded on successively finer silicon carbide papers, then mechanically polished with 1 μm diamond paste and cleaned with ethanol. Oxidation kinetics were determined by continuous isothermal thermogravimetry tests in the temperature range 600–800 °C for exposures up to 100 h. At 800 °C, exposure time was reduced to 20 h because the high mass gain of samples implied the risk of exceeding the maximum weight range of the microbalance. Oxidation tests were carried out under dry synthetic air (dewpoint below –40 °C).

The characterization of oxidation products was performed on samples used for mass gain determination, as well as on samples isothermally oxidized for different exposure times. Cross sections were prepared by conventional metallographical techniques. To prevent scale loss during the metallographic preparation of the sample, the surfaces were coated first with a thin gold layer (by sputtering) and then with a thicker layer of copper (electrolytically deposited). Surfaces and cross sections of the oxidized specimens were studied by scanning electron microscopy (SEM). Phase identification of the oxide scale was performed by X ray diffraction (XRD) using Co Kα radiation and energy dispersive X ray microanalysis (EDX).

3. Results

3.1. Microstructure

Fig. 1 shows transverse and longitudinal views of the tungsten rod. The columnar structure was revealed by etching the surfaces with Murakami’s reagent (modified A). The microstructure consisted of anisotropic elongated grains oriented along the axis of the rod (see inset on Fig. 1). The grain orientation in coupons was perpendicular to the major surfaces, which corresponds to current ITER specifications for the use of tungsten as material in PFCs [8,24].

3.2. Oxidation kinetics

The mass gain curves in dry air at 600, 700 and 800 °C of tungsten processed by conventional techniques are shown in Fig. 2. Mass gain curves clearly proved that the oxidation resistance of pure tungsten decreases substantially above 600 °C. The kinetics were determined by adjusting the mass gain curves to a power law of the form \( \Delta W = k t^n \) (\( \Delta W \) is the mass gain per unit area, \( k \) the oxidation rate constant, \( n \) the rate exponent, and \( t \) the exposure time). Changes in the kinetics laws governing the oxidation behavior could be noticed in the course of the exposure at a given temperature, as presented in Table 1. The oxidation kinetics at 600 °C were governed by almost parabolic laws, \( n \approx 0.7 \), beyond the initial transient state. At 700 °C a significant increment in the mass gain was measured, about one order of magnitude higher than the measured at 600 °C (135 against 11.3 mg cm⁻² respectively). During the initial stages of oxidation at 700 °C the material still followed the almost parabolic behavior found at 600 °C. However, a progressive deviation of the initial almost parabolic behavior toward a nearly linear law was observed after the first 2 h of exposure. The kinetics at 800 °C obeyed linear laws from the initial stages of oxidation. It is interesting to note the mass gain after 20 h of exposure was comparable to that of the sample tested at 700 °C for 100 h.

3.3. X ray diffraction

Three oxides with monoclinic crystalline structure (WO₃, W₁₉O₄₉ and WO₂₉₂) were identified after exposure at 600 °C, as shown in XRD pattern of Fig. 3a. The most intense phase corresponded to WO₃. The peaks assigned to WO₂₉₂ had an intermediate intensity, suggesting that this oxide was probably located in the innermost part of the oxide scale. It is worth noting that the oxide on the surface showed a yellowish color at this temperature, which coincides with WO₃ color.

Major difference of XRD patterns at 700 °C arose from the absence of W₁₉O₄₉ and WO₂₉₂ peaks (Fig. 3b). Absence of both oxides could be attributed to the limited penetration of X ray in a dense material with a high atomic number such as tungsten oxides, as well as the large thickness of the outer WO₃ layer. No formation or disappearance of these oxides in the course of oxidation at 700 °C could be another explanation. XRD patterns at 800 °C were not taken because the irregular growth of the oxide layer (much thicker in the edges than in the center of large smooth surfaces) precluded accurate XRD measurements. Since the structure of the scale at 800 °C for 20 h was similar to that developed after 100 h exposure at 700 °C (see electron microscope observations in the next section), no differences in the nature of the oxides formed.

Fig. 1. (a) Composition of optical microscopy images showing the microstructure of the tungsten bar. (b) Backscattered image showing close magnification of the transverse section. (c) Backscattered image showing close magnification of the longitudinal section.
at both temperatures were expected. This agrees with XRD measurements in the literature which found the same oxides during oxidation at 700 and 800 °C [15].

3.4. Oxidized surfaces

Fig. 4 shows the surface of the scale after oxidation tests. At all temperatures, the external oxide scale was constituted by equiaxed crystals whose size increased with increasing the oxidation temperature. Thus, crystal size ranged between 100 and 200 nm after 100 h at 600 °C and 300–600 nm after exposure for 20 h at 800 °C. During cooling from 700 °C to room temperature, cracking of the scale took place and the scale partially spalled off during subsequent handling. Detachment proceeded along preferential planes parallel to the surface, conferring a stratified appearance to the surface. Significant differences were noticed among detached and non-detached regions. At low magnifications numerous interconnected cracks could be observed over the entire surface of detached regions (innermost part of the scale), as shown in Fig. 5a. On the other hand, some large cracks and incipient non-interconnected secondary cracking were found in non-detached regions, as shown in Fig. 5b. Cracking could be either related to the large volume change associated with oxide formation or could be induced by thermal stresses generated during cooling. Analyses on the surface of detached and non-detached regions also evidenced changes in the structure and morphology of the scale. Thus, the outer scale was relatively dense, excluding the regions with cracks, and constituted by equiaxed grains with sizes ranging between 150 and 400 nm after 100 h of exposure (see Fig. 4b). On the other
hand, spalling permitted to distinguish the porous nature of the inner oxide scale, as shown in Fig. 5c. Crystal size of this inner oxide was coarser, between 200 nm and 1 µm, than that corresponding to the outermost oxide.

Similar features were found after exposure at 800 °C for 20 h, although no spalling took place during cooling. As seen in the sample oxidized at 700 °C, big cracks and non-interconnected secondary cracks were also present on the surface. Observation of the oxide scale on the edges proved the non-equiaxed nature of oxide crystal, as shown in Fig. 6. The columnar morphology of the oxides can be clearly checked, with lengths up to 2–3 µm, leaving numerous cavities during their growth. Therefore, the equiaxed appearance on the external surface arose from the normal view of oxide crystals with respect to the growth direction.

3.5. Cross sectional views

Fig. 7 shows a relatively dense oxide scale of about 50 µm formed after exposure for 50 h at 600 °C. The oxide scale seems to be composed of two layers; a thin outermost layer of about 8 µm and a thicker innermost layer of about 40 µm. The existence of a nearly continuous band of cavities between both layers clearly depicts both parts of the scale. Some cavities also extend from the boundary between both layers towards the gas surface. Moreover, some of the isolated pores in the outermost layer are aligned along the same direction, as marked by the line in Fig. 7. Just beneath the boundary, in a region of about 10 µm, the innermost layer contains abundant voids and porosity. Some of them coalesce to produce large cavities although they are not connected. Underlying this region the layer becomes denser, with very little porosity. Nevertheless, voids and large cavities are again concentrated during further growth. The structure of the oxide layer formed after 100 h of exposure is identical to that observed for 50 h, as shown in Fig. 8. The thickness of the oxide scale is about 95 µm. The scale may be divided into the same two layers. The structure and thickness of the outermost layer (about 10 µm) are practically identical to that found after 50 h of exposure. This clearly indicates that the oxide scale grows by inward oxygen diffusion. On the other hand, the innermost layer thickens steadily in the course of the oxidation. Once more this layer consists of alternating regions with low and high pores, voids or cavities. Either cracks running throughout the oxide scale from the oxide/metal interface to the gas/oxide interface or cracks running parallel to the oxide/metal interface are observed.

Figs. 9 and 10 show the oxide layer formed at 700 and 800 °C, respectively. Both layers have a stratified structure. At 700 °C, a porous structure 800 µm thick formed beneath the compact outer
Cross sectional view of the scale developed on the edges of the sample oxidized in air after 100 h exposure at 800 °C.

Fig. 6. Cross sectional view of the scale developed on the sample oxidized in air after 20 h exposure at 800 °C.

Cross section of the scale developed on the sample oxidized in air after 50 h exposure at 600 °C. The inset shows a detail of the oxide scale.

Fig. 7. Cross section of the scale developed on the sample oxidized in air after 100 h exposure at 600 °C. The inset shows a close magnification of the scale.

Layer of not more than 10 μm in thickness. At 800 °C, the scale thickness reaches 1.15 mm. Each layer within the stratified structure is separated from each other by interconnected cavities. Although the test at 800 °C was only carried out during 20 h, the thickness of the oxide scale is 1.5 times larger than that of the scale formed at 700 °C after 100 h of oxidation.

4. Discussion

The results evidence the complexity of tungsten oxidation. This agrees with the numerous discrepancies reported in the literature concerning kinetics, composition, and structure of the oxide scale [14–23]. Although the change from parabolic to linear kinetics has been described during oxidation in the temperature range 500–700 °C [14,18], a parabolic behavior was not found in our study over the entire temperature range. Furthermore, our results differ from the data reported in previous works in which kinetics obeyed parabolic laws during short term exposure in the interval 400–900 °C [14,20,25]. This means that the oxide scale was unable to provide effective protection from the early stages of oxidation, as deduced by the lateness for achieving the steady state. More over, mass gain rate was increased after exposure for 6 h, as marked in the mass gain curve of Fig. 11. This suggests that the slight protective nature of the initial scale was lost after this period. Additional time was required for recovering the healing nature of the oxide scale until new impairment of the scale took place (at about 50 h). Then, a new steady state would be attained until a new event of protectiveness loss would take place.

XRD data proved that the scale at 600 °C consisted of different oxides with the following sequence, from the outer surface towards the inner metal, WO3, W18O49 and WO2.92. The yellow color of external oxide confirmed that WO3 was mostly located in the outer part of the scale. This coincides with some studies reported in the literature [14,15,18,21,26]. Nevertheless, other authors have described the formation of a protective dark layer [15,20,21,26]. Discrepancies could result from the different exposure times used in these works. Moreover, the influence of impurities cannot be ruled out because the reduction kinetics of non sag (NS) doped tungsten blue oxide is affected strongly by small amounts of impurities such K, Al or Si [27]. Usually, the typical yellow color of WO3 was not observed during short term exposures, up to 6 h, between 500 and 700 °C [14], which would confirm that WO3 formed once a continuous dark layer was established. Kellet et al. attributed it to W18O49 oxide [15]. Furthermore, Webb et al. found a dark blue layer, presumably W4O11, after scraping the
Cross sectional views revealed a relatively dense scale, but curiously, a nearly continuous band of cavities, many times interconnected, was present underlying the outermost external layer. Formation of these cavities was, obviously, related to the first point in the mass gain curve at 600 °C where an increase in the oxidation rate was observed. Microcracking in the WO₃ layer has been suggested to promote the change from parabolic to linear laws because of the formation of transversal cracks throughout the scale [14]. Cracking of the oxide scale could be expected because of the significant volume change resulting from the oxidation of tungsten into any kind of tungsten oxide (Pilling Bedworth ratio of 3.3 for WO₃). The high compression stresses arising from oxide growth were stored in the scale and mostly released during cracking events. Although some transversal cracks could be also found crossing thoroughly the oxide scale, the absence of localized attack in the metal, ahead the crack tip, implies that accelerated oxide growth cannot be associated with transversal cracking. Probably, these transversal cracks could be originated by the stresses generated during cooling as a result of: (i) large differences among their expansion coefficients of tungsten and tungsten oxides and/or (ii) volume changes induced by allotropic transformation of tungsten oxides. At the temperatures used in this work, the orthorhombic structure transformed into monoclinic WO₂ during cooling. The volume change (ΔV) can be calculated as ΔV = (V_{mon} - V_{ort})/V_{ort}. Taken V_{ort} = 430.90 and V_{mon} = 146.69 from XRD standard patterns of monoclinic (pattern 00 054 0508) and orthorhombic WO₃ (pattern 01 071 0131), ΔV = 0.66 (shrinkage of 66%).

The oxidation was divided into different stages, illustrated in the scheme of Fig. 13. Basically, growth stresses induced during oxidation were released by cracking of the scale. This cracking was limited to a small restricted region. In these regions two processes or phenomena occurred simultaneously. In the neighbor non cracked region, oxidation proceeded normally. New oxide formation was accompanied by a considerable volume increase which could be accommodated by moving the scale outwards. Although oxygen transport across the crack occurred quickly, some time was required before oxygen could be transported from the top side to the bottom side of the crack. In the meantime, the scale shifted continuously outwards, leading to crack enlargement in such a way that cracks tended progressively to appear as voids or cavities. The enlargement of voids was halted when new oxide formed at the bottom side of cavities. At this point, oxide continued to form as a continuous layer until growth stresses were again released through local cracking events. This mechanism explains the multi layered appearance of the scale in which a porous band was followed by a relatively dense layer.

Impairment or cracking of the oxidation scale led to the change in the structure of the oxide underlying this region. The structure became columnar, with grains orientated perpendicularly to the scale/substrate interface. This configuration facilitated rapid

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**Fig. 10.** Cross section of the scale developed on the sample oxidized in air after 20 h exposure at 800 °C. The inset shows the sample after oxidation test.

**Fig. 11.** Mass gain curve of the sample oxidized 100 h at 600 °C in dry air. Arrows indicate points at which protective nature of the scale was lost.

external yellow scale in a sample oxidized 4 h at 700 °C [20]. Other authors concluded that this layer corresponded to WO₂ [26]. To check this point, a sample was oxidized for 1 h. Visual aspect of the sample evidences a black thin layer. XRD pattern of Fig. 12, taken with an incidence of 5°, proved that maximum intensity peak corresponded to W₁₈O₄₆. Intense WO₂.₉₂ peaks were already present (right and left shoulders of the most intense peaks) after this short exposure time.

**Fig. 12.** XRD pattern (incidence angle of 5°) of tungsten sample oxidized at 600 °C for 1 h in dry air. ◆, W₁₈O₄₆. ●, WO₂.₉₂. ×, W. The inset shows the black film formed on the sample after the oxidation test.
porous scale whose morphology resembled quite well that of the multilayered scale developed during oxidation of pure titanium above 800 °C [28,29]. Unlike the rutile scale formed on pure titanium, the continuous disruption or crack between individual layers was absent. Large cavities, sometimes connected, appeared instead. This agreed rather well with the mechanism proposed by Gulbransen and Andrews [14]. According to these authors, oxygen diffusion proceeded through a cyclic mechanism involving periodical cracking at local areas when a dense oxide layer attained a critical thickness. The size of cavities was larger as temperature was increased, indicating that new oxide growth at metal/oxide interface took place faster than pressure increase inside the crack to form new oxide at the bottom of the crack. The result is the enlargement of cavities embedded in the scale.

XRD patterns at 700 °C did not confirm the presence of WO2.92. Such absence could be attributed to: (a) WO2.92 was located internally, far from the surface and consequently out of the detection range of X ray or (b) WO2.92 was transformed progressively into WO3 in the course of the oxidation. To check this point the scale formed at 700 °C was detached from the surface and, then, pulverized. The only phase detected in the powder was WO3. This proved that WO2.92 transformed into WO3 when oxidation obeys linear kinetics. It is interesting to note that the oxide scale grows strongly outwards at 800 °C, as presented in the inset of Fig. 10. Although the total mass gain was very similar to the sample oxidized at 700 °C, the thickness of the scale was significantly larger, about 330 μm. The latter indicated the lower compactness of the scale developed at 800 °C. This agreed with microstructural features observed in the scale as the maximum size of cavities was around 13 and 19 μm at 700 and 800 °C, respectively.

As was commented in the preceding discussion, the outer scale was always constituted by WO3. The dark blue oxide formed after short exposure times indicated that W18O49 was formed from the initial stages of oxidation whereas WO3 grew later. WO3 required outward tungsten transport from the metal to the outer surface. Since rapid oxygen entrance to the metal/oxide interface consumed all tungsten, outward tungsten diffusion should be negligible. In addition, high volume of tungsten atoms and low oxidation temperature should make it unexpected. Therefore, other mechanism should account for outward tungsten transport. Transport as volatile tungsten oxide, probably, might be the most reasonable alternative. The stability of tungsten oxides is highly dependant on oxygen pressure, leading to the formation of oxides with different stoichiometries. Removal of oxygen from WO3 results in lower oxides (WO3-x, 0 < x < 1). The lower the oxygen partial pressure the lower the stoichiometry. At 700 and 800 °C, the pressure dependence is as follows; WO3, WO2.92, W18O49 and WO2 [30]. Initial formation of W18O49 should fix the oxygen gradient entering into the metal substrate. Therefore, WO2.92 formation should be unexpected unless the oxygen partial pressure would rise up to the level in which WO2.92 could grow. These conditions would be achieved when cracking of W18O49 layer occurred and the oxygen pressure in cavities was increased. Then, oxygen pressure could rise up to the point that WO2.92 could volatilize before transformation into WO3 would take place. This WO3 should be transported outwards, towards the outer surface. There, the increase in the oxygen pressure should promote deposition.

5. Conclusions

From the present work the following conclusions can be drawn:

1. The oxidation was initially controlled by the development of a continuous W18O49 layer. Increase in the oxidation rate towards linear kinetics is due to local cracking of W18O49 layer.
2. At 600 °C, the scale provided some protection to pure tungsten because massive cracking was limited to very few events clearly viewed in mass gain curves. At 700 and 800 °C, oxidation proceeded through a cyclic mechanism involving periodical cracking at local areas when a dense oxide layer attained a critical thickness.

3. Equiaxed structure of W18O49 layer changed to the columnar structure of the thick WO2.92 formed after cracking of W18O49 layer. WO2.92 was progressively transformed into WO3 in the course of the oxidation.

4. WO2.92 Volatilization transported tungsten outwards, towards the gas surface, leading to the formation of the yellow external WO3 layer.

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