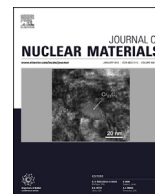




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Formation of oxide layers on tungsten at low oxygen partial pressures

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ABSTRACT

This work focuses on the oxidation of tungsten in inert gas atmospheres containing oxygen and moisture. It is particularly relevant for the European Spallation Source where the tungsten target is cooled by purified helium gas and the 5 MW proton beam can raise the maximum target temperature beyond the threshold for oxidation. Tungsten discs were oxidized isothermally at 400° to 900 °C for 2 h in pure helium and helium mixed with oxygen and water vapor, with varying partial pressures up to 500 Pa. Tungsten was oxidized even with a small amount of oxygen (≤ 5 ppm) present in industrially pure helium. Non-isothermal oxidation of tungsten foils was carried out in water vapor (~ 100 Pa), *in situ* in an environmental scanning electron microscope. On specimens oxidized in inert gas containing water vapor (2 h, $p_{H_2O} \sim 790$ Pa), Auger electron spectroscopy studies confirmed the presence of a thin oxide layer (40 nm) at 400 °C. At 500 °C the oxide layer was 10 times thicker. A dark, thin and adherent oxide layer was observed below 600 °C. Above this temperature, the growth rate increased substantially and the oxide layer was greenish, thick and porous. Oxide layers with varying stoichiometry were observed, ranging from WO_3 at the surface to WO_2 at the metal-oxide interface. For comparison, oxidation of tungsten alloys in He-5% O_2 was studied. The implications of this work on the design and operation of the helium loop for cooling the target are discussed.

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1. Introduction

This study focuses on the oxidation behavior of alloyed and unalloyed tungsten at elevated temperatures, in a helium atmosphere containing small amounts of oxygen and moisture present as impurities. This is of particular interest to the European Spallation Source (ESS) which has chosen to use unalloyed tungsten as the spallation material. The target is designed as a rotating wheel carrying tungsten bricks of the size $80 \times 30 \times 10$ mm. The rotation is synchronized with the 14 Hz pulse of the 2 GeV proton beam. The duration of each beam pulse is 2.86 ms with a 62.5 mA beam current, providing 5 MW time averaged beam power to the target with a 4% duty factor. The heat generated in tungsten from the beam/material interaction is cooled by active helium flow, with the

maximum temperature in the target reaching 450 °C. Although helium is an inert gas, the incidental presence of small amounts of oxygen and moisture can lead to oxidation and erosion of the target.

The spallation process produces a large amount of radioactive isotopes, fast neutrons and highly penetrating gamma radiation [1], thus making safety issues a top priority. One particularly important issue is the formation of highly volatile, radioactive tungsten hydroxides which can potentially be released into the surroundings under accidental conditions. Such a major event could be triggered by overheating of the target, caused for example by an incidentally over-focused beam [2]. If the higher beam intensity is not corrected in time, it can cause the target vessel to lose its function of helium coolant confinement, which would expose the overheated tungsten to an oxidizing environment, and allow for the release of radioactive isotopes in forms of gas, aerosol and volatiles. A similar incident can occur in the case of loss of coolant in the target. Since the decay heat in the tungsten will drive the temperature up, engineering efforts have been made to secure a passive cooling path to

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keep the tungsten below the onset temperature of tungsten oxide sublimation [3].

1.1. Present work

The main objective of this study is to understand the oxidation characteristics of unalloyed tungsten in gaseous atmospheres and temperatures of relevance to ESS, during normal as well as off-normal operating conditions. The design lifetime of the target wheel is five years under 5 MW beam power. During normal operation, the tungsten will reach temperatures above 400 °C, which is close to the temperature at which the rate of oxidation becomes significant. The helium loop for the target cooling has a purification system to keep the oxygen and moisture levels low; however, there is a risk that even a small impurity level of oxygen and vapor could be enough to oxidize the tungsten. For an efficient design of the target primary cooling loop, it is important to understand the oxidation characteristics of tungsten in such gaseous environments. It is also important to identify the temperature at which the oxide transitions from the adherent and protective type to the porous, non-protective one with a significantly higher growth rate.

Although oxidation of tungsten at high temperatures has been studied extensively by Gulbransen and co-workers [4–9] and most recently by Greene and Finfrock [10,11], these studies are restricted to oxygen and steam-rich atmospheres. There is not much information in the literature on the oxidation of tungsten at low oxygen partial pressures and at relatively low temperatures. Hence, the present study was taken up to gather oxidation data for unirradiated unalloyed tungsten (400°–900 °C) in inert gas mixtures containing small amounts of oxygen (p_{O_2} : 0.5 Pa to 5.1 kPa) or steam (p_{H_2O} : 100–790 Pa). For purposes of comparison, the oxidation behavior of a few tungsten alloys has also been studied in this work.

1.2. Literature review

Tungsten is characterized by a high density, extremely high melting point and good strength at high temperatures. However, a major drawback is its poor resistance to oxidation which limits the use of uncoated tungsten as a structural material at elevated temperatures. Tungsten is oxidized even at relatively low temperatures [12], and the rate of oxidation becomes significant above 600 °C [13]. At even higher temperatures the oxide becomes volatile. The oxidation process is relatively complex, owing to the wide range of oxides formed with varying stoichiometries, and to the volatility of the oxide. Consequently, the results reported in the literature on the kinetics, composition and structure of tungsten oxides vary widely [14].

A phase diagram for the W–O system [15] is presented in Fig. 1. The diagram shows the presence of stoichiometric oxides (WO_2 and WO_3) and a number of non-stoichiometric oxides corresponding to the formula WO_{3-x} where $0 < x < 1$. The composition and stability of the non-stoichiometric oxides are strongly dependent on the partial pressure of oxygen. Despite the large number of oxides found in the W–O system, the most commonly encountered ones are WO_2 , $WO_{2.72}$ ($W_{18}O_{49}$), $WO_{2.9}$ ($W_{20}O_{58}$) and WO_3 [8,16].

The oxides exhibit colors from yellow to green to dark blue; WO_3 (yellow), $W_{20}O_{58}$ ($WO_{2.9}$, dark blue), $W_{18}O_{49}$ ($WO_{2.72}$, violet) and WO_2 (chocolate brown). The color changes are related to a loss of oxygen in the original WO_3 structure, generating an additional valence state and cation to cation charge transfer between W^{6+} and a reduced ion [17,18].

1.2.1. The different stages of oxidation

The oxidation of tungsten proceeds through several distinct

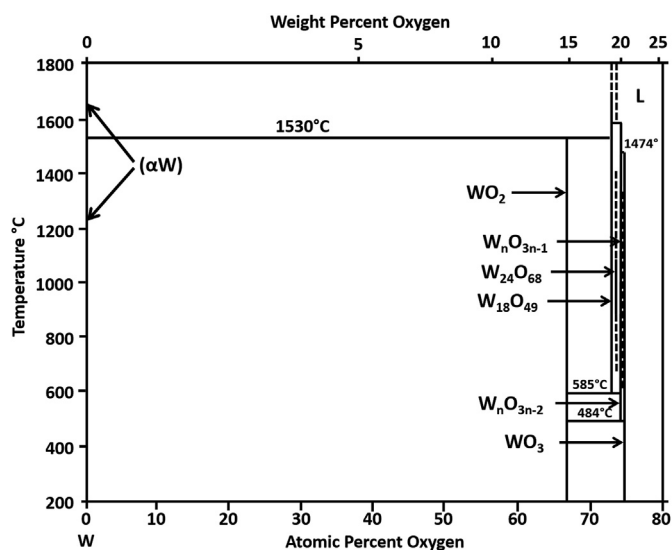


Fig. 1. The W–O system [15].

steps which are governed by different mechanisms. The initial oxidation is phase boundary controlled, with no diffusional effects assuming no limitation on oxygen transport in the gas phase. During the initial stages of oxidation, for thin oxide layers (2–4 nm) and low temperatures (<400 °C), the oxide growth rate follows the logarithmic law [19]. At slightly higher temperatures and thicker oxide layers, the parabolic law governs the oxide growth. A protective film is formed and the rate is limited by the diffusion of O^{2-} ions through the oxide scale. At this stage, the oxide layer on tungsten is often very thin, adherent and protective, thus limiting further oxidation. Different compositions have been reported for this layer, such as WO_2 [5], $WO_{2.75}$ [20], and $WO_{2.72}$ [8,13].

The second stage of oxidation has been observed between 500° and 700 °C, involving the growth of the dark layer as well as the formation and growth of a bright yellow oxide layer. The yellow oxide consists of WO_3 which is usually found in the outermost layer where the oxygen content is the highest. Oxygen ion vacancies play an important role in the growth of WO_3 . Sikka and Rosa [21] confirmed this view with oxidations experiments in which Pt-wire markers moved from the oxide/metal interface toward the oxide/gas interface, showing the inward diffusion of oxygen ions through the oxide. Cifuentes et al. [22] observed that the oxidation was initially controlled by the formation of a continuous $W_{18}O_{49}$ layer which cracked eventually, leading to a higher oxidation rate and linear kinetics. Thick and columnar $WO_{2.92}$ formed on the cracked $W_{18}O_{49}$ layer, followed by the formation of the yellow WO_3 layer on top.

The next stage of the oxidation process occurs when the WO_3 has covered the surface of the thin dark film. Being porous, not particularly adhesive and having a Pilling-Bedworth ratio of 3.35, this oxide creates high stresses causing the oxide layer to crack and thus exposing new surface to the oxygen. The non-protective nature of WO_3 results in a linear oxidation rate.

1.2.2. Reaction with steam and oxide sublimation

At higher temperatures, the oxide becomes volatile. The onset temperature is related to pressure, moisture and oxygen content of the gas, gas flow rate, and oxide film thickness [7,10,11,23]. The lowest reported onset temperature for sublimation of tungsten oxide (in 100% steam) is in the range 700°–800 °C [11]. Numerous reports suggest that any moisture content in the atmosphere will enhance the volatility and speed up the oxidation process [24], as

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