F Klein et al.

Sublimation of Advanced Tungsten Alloys Under DEMO Relevant Accidental Conditions

Preprint of Paper to be submitted for publication in Proceeding of 30th Symposium on Fusion Technology (SOFT)

Sublimation of Advanced Tungsten Alloys Under DEMO Relevant Accidental Conditions

Felix Klein[a], Andrey Litnovsky[a], Tobias Wegener[a], Xiaoyue Tan[a,c], Jesus Gonzalez-Julian[a], Marcin Rasinski[a], Janina Schmitz[a,b], Christian Linsmeier[a], Martin Bram[a], Jan Willem Coenen[a]

[a]*Forschungszentrum Jülich GmbH, Institut für Energie- und Klimaforschung, 52425 Jülich, Germany*
[b]*Department of Applied Physics, Ghent University, 9000 Ghent, Belgium*
[c]*School of Materials Science and Engineering, Hefei University of Technology, Hefei, 23009, China*

Abstract

Tungsten (W) is deemed as the main candidate for the first wall armor material of future fusion power plants such as DEMO. Advantages of W include a high melting point, low erosion yield, low tritium retention, and a high thermal conductivity. One issue concerning W is the oxidation resistance in case of a loss-off-coolant accident with simultaneous air ingress. The major challenge in such a scenario is to control the sublimation which is responsible for a release of radioactivity. This work studies an alloy containing tungsten (W), 12 weight % chromium (Cr), and 0.6 weight % yttrium (Y) in DEMO-relevant conditions: a temperature in the range of 1100 K to 1473 K in humid air. The sublimation rates are measured for the first time in humid air. Tungsten oxide sublimates at a rate of $1 \times 10^{-4}\,\mathrm{mg\,cm^{-2}\,s^{-1}}$ at 1273 K in humid air. At the same conditions the alloy suppresses sublimation by more than one order of magnitude as compared to that of pure W. This suppression is achieved due to the formation of a protective chromium oxide layer on the surface of the sample. Details about the protection mechanisms are presented and discussed.

Keywords: Tungsten alloys, W-Cr-Y alloys, Oxidation resistance, Sublimation, DEMO, Humidity, Accident

1. Introduction

Future fusion power plants require the development of a first wall armor material withstanding extreme particle and radiation loads [1, 2]. Considering safety, the formation of long-lived radioactive isotopes when irradiated with neutrons and a tritium inventory has to be prevented [3]. As tungsten (W) meets these safety requirements, has a low erosion rate, high melting point, and high thermal conductivity, it is a promising candidate for the first wall armor [4].

Besides embrittlement of tungsten [5], there is another important safety consideration: in a loss of coolant accident (LOCA), cooling systems fail and air ingress into the vacuum vessel may occur. Due to the nuclear decay heat, temperatures in the range from 1200 K to 1450 K for several weeks are predicted in such a scenario [6]. The radioactive W oxidizes and volatilizes, posing a severe hazard for the environment [7]. For a successful future fusion power plant like DEMO, a new material is required. The new material should preserve the advantages of W coupled with suppressed sublimation in case of an accident.

Different elemental compositions and manufacturing routes were tested [7, 8, 9]. The alloy containing tungsten (W), 12 weight % chromium (Cr), and 0.6 weight % yttrium (Y) (in the following written as W-12Cr-0.6Y) consolidated by Field Assisted Sintering Technology shows promising results: during exposures to deuterium plasma, erosion yields are similar to pure W [10]. Moreover, the oxidation resistance is significantly improved: complete mechanical destruction is avoided for at least three weeks [11].

Previous studies on bulk alloys focused on testing and development in dry atmosphere [11, 12, 13, 14]. Humidity was only considered in one study on thin films [15] which do not allow to study long exposure times due to a limited material reservoir [16]. However, both the atmospheric air itself as well as water cooling systems are a potential source of humidity in case of an accident. Therefore, the presence of humidity is likely in case of a LOCA. This paper investigates the oxidation and sublimation of bulk W-12Cr-0.6Y alloys for the first time in humid air. In this paper the term 'humid air' means synthetic air with a relative humidity level of 70 % at 313 K corresponding to 5 volume % humidity.

First, the experimental methods are presented. There is a particular focus on how the contribution of sublimation is measured independently of the oxidation. Second, the results on oxidation and sublimation at 1273 K in humid air are presented and discussed. Third, the limits for application of the present material are investigated by varying the temperature in the range from 1100 K to 1473 K for the first time in humid air.

2. Experimental

The sample production process starts with mechanical alloying, more details on the chosen parameters are found in [12]. The obtained powder is compacted by Field Assisted Sintering Technology (FAST). The main sintering parameters are the heating rate of $200\,\mathrm{K\,min^{-1}}$, a pressure of 50 MPa, a maximum sintering temperature of 1740 K, and a holding time at the maximum sintering temperature of 0 s to 30 s. More details on the sintering process and reasons for the chosen parameters are writ-
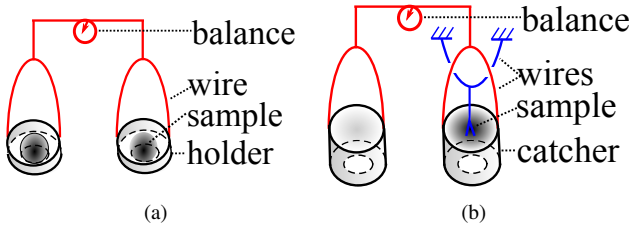

Figure 1: Schematic of the measurement for oxidation and sublimation. (a) The sample is placed directly into a holder and the mass change of the sample is recorded. (b) The sample is hung into a catcher, without direct contact, and the mass change of the catcher is recorded.
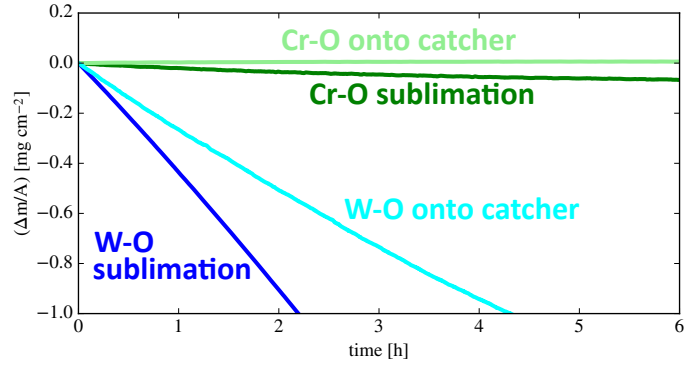

Figure 2: Calibration measurement of the catcher at 1273 K in humid air. There are two setups: First, a fully oxidized sample is placed into the holder and the mass change due to sublimation is measured. Second, a sample is hung into the catcher and the mass gain of the catcher due to deposition of sublimated material is set to the mass loss of the sample.

ten in [11]. After sintering the samples are ground with a surface finish using P1200-grade silicon carbide abrasive paper.

The carbon (C) content of the samples is determined using the device Leco CS600. The material is combusted in a stream of purified oxygen and the C content is determined by the infrared absorption.

The microstructure of the samples is characterized using the Carl Zeiss CrossBeam XB540, a combined Scanning Electron Microscopy (SEM) and Focused Ion Beam (FIB) system equipped with Energy Dispersive X-ray analysis (EDX) and an In-lens Energy-Selective-Backscatter detector (ESB). Before making FIB cuts, a layer of platinum (Pt) is locally deposited onto the sample to avoid damage of the surface of the sample.

Oxidation and sublimation are measured using the thermogravimetric analyzer TAG-16/18 from Setaram. Measurement of oxidation and sublimation requires two measurements of two identical samples. In the first setup as illustrated in Fig. 1 a, the sample is placed into an alumina holder and the mass change of the sample relative to an inert product compensating for buoyancy effects is measured. This measurement yields the total mass change of the sample - the sum of mass gain due to oxidation and the mass loss due to sublimation. The second setup is illustrated in Fig. 1 b. The sample is hung into an alumina catcher. Sample and catcher have no mechanical contact. Material sublimating from the sample can deposit onto the catcher, causing a mass increase which is measured.

Calibration to determine what fraction of the sublimated material deposits onto the catcher is carried out in the following way at 1273 K in humid air: films of pure W and pure Cr with a thickness a few micrometers are deposited onto a substrate using magnetron sputtering. The films are fully oxidized. These oxides are placed into the holder setup as shown in Fig. 1 a, and the mass loss due to sublimation is measured. The results of the sublimation measurements are shown in Fig. 2. Sublimation rates of 1×10^{-4} mg cm^{-2} s^{-1} and 2×10^{-6} mg cm^{-2} s^{-1} are found for W and Cr, respectively.

In a second experiment bulk samples of pure W and pure Cr are hung into the catcher also at 1273 K in humid air. The mass increase of the catcher, corresponding to mass loss of the sample, is found to be 6×10^{-5} mg cm^{-2} s^{-1} for W and -3×10^{-8} mg cm^{-2} s^{-1} for Cr, see Fig. 2. The rate for Cr is within the measurement uncertainties of the micro-balance. Theses rates can be compared with the rates measured with oxides. It can be concluded that around half of the sublimating

tungsten oxide deposits onto the catcher whereas the deposition of chromium oxides is below the detection limit.

3. Oxidation and Sublimation at 1273 K

Characterization of the samples after sintering and grinding yields a grain size of around 0.2 μm with yttria particles of 10 nm to 20 nm at the grain boundaries, as seen in the cross section imaged by SEM shown in Fig. 3 a. The C content is 2×10^2 ppm. For pure W such an amount would yield an increase of the ductile to brittle transition temperature of several hundred kelvin [17]. The consequences of C impurities on W-Cr-Y alloys are not yet studied systematically. However, the amount of C should be reduced anyways due to ^{14}C activation [3]. One approach to reduce the C content could be using W-foil instead of C-foil to pack the powder into the die during sintering.

EDX spectra on the surface after 10 days of oxidation in humid air, see Fig. 3 b, show 37 atomic % Cr, 62 atomic % O, and 0.3 atomic % W. Thus, a protective Cr_2O_3 layer forms on the surface. Fig. 3 c shows an overview image of the surface. The lamella-like structure in the 'thick' region indicates that multiple layers are above each other. Only in the 'thin' region a single layer of Cr_2O_3 is found.

Cross sections are cut in both regions: in the 'thin' region, see Fig. 3 d, a closed protective oxide layer with a thickness of 2.8 μm is found on the surface. Below the metal internal Cr_2O_3 is found. In the 'thick' region a Cr_2O_3 layer with a thickness beyond the cutting depth of the crater is found, see Fig. 3 e. The observed pores coincide with the lamella like structure seen in Fig. 3 a. The brighter spots within the Cr_2O_3 are identified as W-Y-oxide using EDX. Graphical image analysis of the contrast on in Fig. 3 e yields that around 5 % of the cross section is covered with W-containing oxide. However, the W-containing oxide is trapped within the Cr_2O_3, thus not posing a radiological hazard.

W-containing oxides on the surface may sublimate in contrast to the trapped oxides. The oxides on the surface are quantified using ESB, resolving contrast even on the non-polished oxide
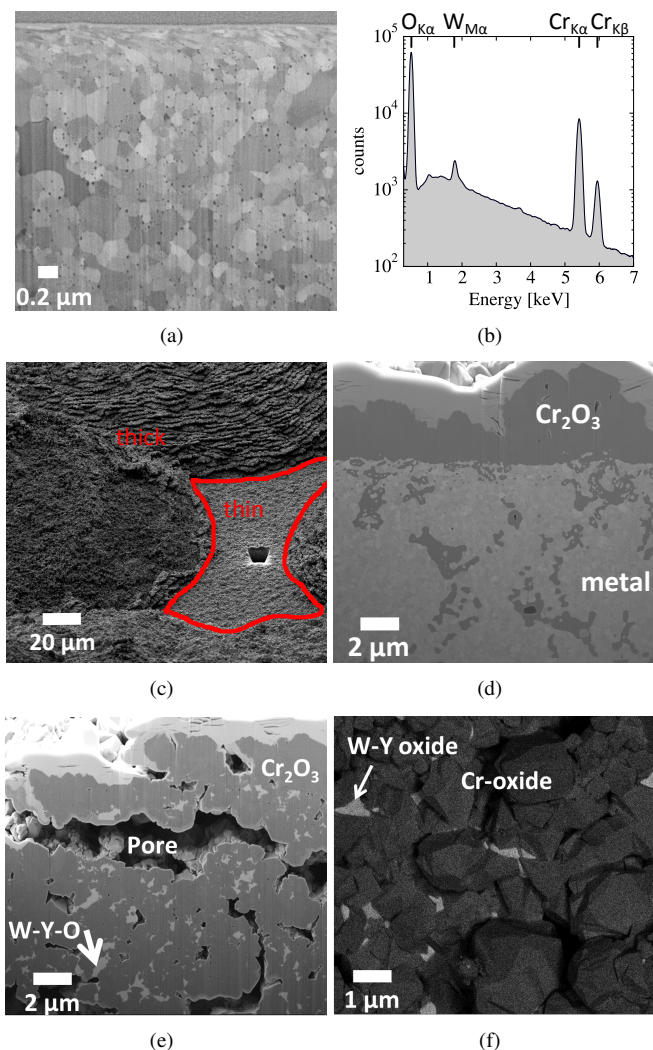
2

Figure 3: Microstructure shown by electron microscopy images: (a) Cross section of the material after sintering. (b)-(f) shows microscopy after oxidation for 10 days at 1273 K in humid air: (b) an overview surface image with regions 'thin' and 'thick', (c) a cross section in the 'thin' region, (d) a cross section in the 'thick' region, (d) a high magnification ESB image with a grid voltage of 1 kV resolving both W-Y oxide and Cr-oxide representative for regions 'thin' and 'thick', and (e) an EDX spectrum on the surface.

surface. An exemplary ESB image is shown in Fig. 3 f. Graphical analysis of seven images on randomly selected spots on the surface of the sample yield a surface coverage of 1 ± 0.8 % with W-containing oxides.

Such a strong suppression of W-oxide formation was not observed in previous studies conducted in dry air [11], despite the fact that samples from the same production route were used. The reason is the presence of water in the atmosphere of the experiments in the present study. Oxidation is mainly caused by the dissociation of water [18]. H_2O has a Gibbs free energy of -353 kJ mol^{-1} at 1273 whereas Cr_2O_3 has a Gibbs free energy of -530 kJ mol^{-1} [19]. Thus, the water reacts with the Cr leaving free H. Once there appears an excess amount of O the oxygen has two options: it can react with W or with H. The Gibbs free energy of WO_3 is -347 kJ mol^{-1} which is less negative than the

one of water [19]. Thus, WO_3 is only formed if not only Cr but also H is depleted. This is a major difference to the studies in dry atmosphere - in the dry case, there is no H which may act as a buffer to suppress the formation of WO_3 until more Cr has diffused to the surface.

The expected sublimation rate can already be estimated based on the aforementioned results: Cr_2O_3 sublimates at a rate $s_{Cr} = 2 \times 10^{-6}$ mg cm^{-2} s^{-1} as shown in Fig. 2. WO_3 sublimates at a rate $s_W = 1 \times 10^{-4}$ mg cm^{-2} s^{-1} as shown in Fig. 2. Since only 1 % of the surface of the alloy is covered with W-containing oxide (see Fig. 3 f), a sublimation rate s can be estimated to

$$s = 0.99s_{Cr} + 0.01s_W = 3 \times 10^{-6} \text{ mg cm}^{-2} \text{ s}^{-1}.$$

The contribution of W is also measured using a second method: oxidation inside a catcher as illustrated in Fig. 1 b. The result is shown in Fig. 4: $s_{Catcher} = 2.3 \times 10^{-7}$ mg cm^{-2} s^{-1} of material from the sample deposit onto the catcher. The calibration in Fig. 2 showed that about half of the tungsten oxide sublimating from the sample deposits onto the catcher. Thus, the sublimation of W-oxide from alloy is measured to be $s_W^A = 2s_{catcher} = 0.5 \times 10^{-6}$ mg cm^{-2} s^{-1}. Here, the contribution of W to the total sublimation rate is half as compared to the estimation based on the ESB-image analysis. The total sublimation rate of Cr-oxide and W-oxide from the alloys can still be estimated to 3×10^{-6} mg cm^{-2} s^{-1}.

There are various measurement uncertainties for both methods: sublimation from the catcher over long times is neglected, the error bar on the surface-coverage with W-containing oxide is rather large, it is assumed that the W-containing oxide on top of the alloy sublimates at the same rate as pure W-oxide. Therefore, a difference of a factor of two on the contribution of W-oxide might be acceptable. The order of magnitude of sublimation from the alloys in case of a LOCA with 1273 K and humid air is determined to be on the order of 10^{-6} mg cm^{-2} s^{-1} using two independent methods.

Fig. 4 illustrates these results by showing

- the mass deposited onto the catcher.

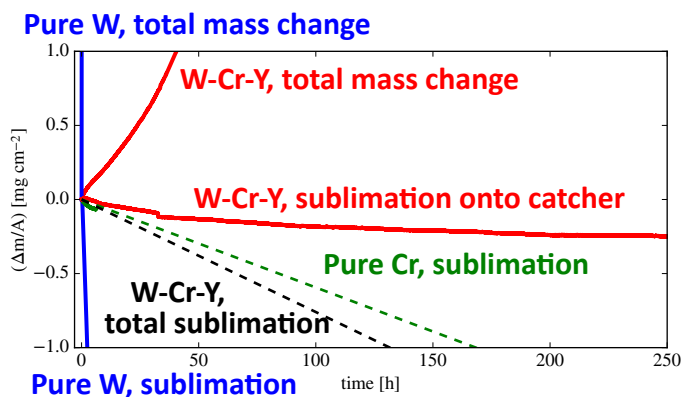- the sublimation of Cr, interpolated from the measurement shown in Fig. 2.

Figure 4: The total mass change of the samples due to oxidation and sublimation, and the contribution from sublimation are shown as a function of time. Measurements are performed at 1273 K in humid air.

- the calculated total sublimation rate of the alloy, which is the sum of the sublimation from Cr-oxide and W-oxide.

- the sublimation of pure W-oxide for comparison.

- the total mass change of the sample for pure W and the alloy. The total mass change is the sum of mass gain due to oxidation and mass loss due to sublimation.

In summary, the main component sublimating is shifted from W to Cr. This change yields a reduction of the sublimating material by more than one order of magnitude assuming a LOCA with 1273 K and humid air. However, it remains an open question on what safety limits are required for a future demonstration fusion power plant and what additional features will be implemented to trap material released to the air inside the vessel.

4. Limits of Application

In order to assess different design concepts for DEMO and the feasibility of the current material it is crucial to measure the behavior of the material at different temperatures. Thus, three identical W-11.4Cr-0.6Y samples are oxidized in humid air at different temperatures for 44 h. The total mass change of the samples is shown in Fig. 5.

At 1473 K mass loss at a rate of 5×10^{-4} mg cm^{-2} s^{-1} is measured after 4 h of oxidation, see Fig. 5. The sublimation rate is even higher as this rate includes the mass gain from oxidation. After 44 h the sample is mechanically destroyed as shown in the photograph.

At 1273 K a linear mass gain of 2×10^{-5} mg cm^{-2} s^{-1} is measured, see Fig. 5. At 1100 K this rate is reduced by a factor of 20 due to the lower temperature. The samples do not exhibit classical passivation as the mass gain is linear and not parabolic. Nevertheless, the sample can withstand the exposure up to 1273 K by forming a protective Cr$_2$O$_3$ layer suppressing the release of W-oxides as shown in section 3. The photographs in Fig. 5 show that the samples can maintain their cubic shape, which is important for the stability of the wall after a LOCA.
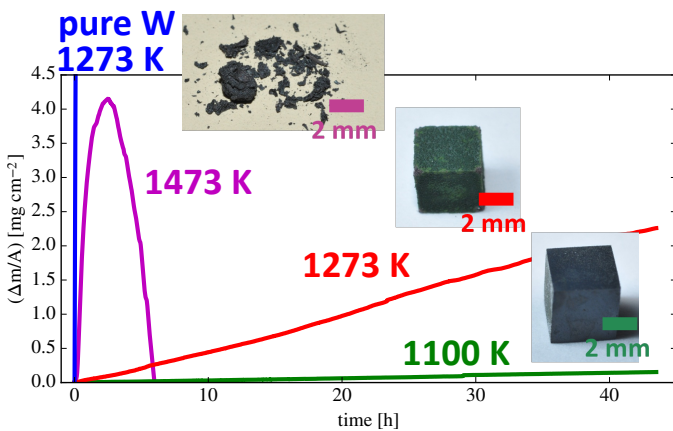

Figure 5: The total mass change of samples due to oxidation and sublimation as a function of time. Measurements are performed in humid air at different temperatures as specified in the figure. All photographs are taken after 44 h of oxidation.

5. Conclusions

The advanced tungsten alloys containing W-11.4Cr-0.6Y are a promising candidate as first wall armor material for future fusion power plants. This alloy provides intrinsic safety in case of a loss-off-coolant accident with simultaneous air ingress up to a temperature of 1273 K.

The influence of humidity on the oxidation resistance has been studied in detail. Two main consequences are found: first, the sublimation rate of Cr$_2$O$_3$ is enhanced in the presence of humidity. Second, the formation of W-containing oxides is almost completely suppressed. The suppression is achieved as a protective Cr$_2$O$_3$ layer forms on the surface. Experimental evidences are given that the material would withstand a LOCA for at least 10 days. The sublimation is dominated by Cr-oxide, the rate will be on the order of 10^{-6} mg cm^{-2} s^{-1} which is a suppression of the release by more than one order of magnitude as compared to pure W. The protection cannot be maintained at 1473 K.

References

[1] Linsmeier, Ch, M. Rieth, J. Aktaa, T. Chikada, A. Hoffmann, J. Hoffmann, A. Houben, H. Kurishita, X. Jin, M. Li, and et al. Development of advanced high heat flux and plasma-facing materials. *Nucl. Fusion*, 57(9):092007, 2017.

[2] J. W. Coenen, S. Antusch, M. Aumann, W. Biel, J. Du, J. Engels, S. Heuer, A. Houben, T. Hoeschen, B. Jasper, and et al. Materials for DEMO and reactor applications - boundary conditions and new concepts. *Phys. Scr.*, 2016(T167):014002, 2016.

[3] M. R. Gilbert, T. Eade, C. Bachmann, U. Fischer, and N. P. Taylor. Activation, decay heat, and waste classification studies of the european demo concept. *Nucl. Fusion*, 57, 2017.

[4] Y. Ueda, K. Schmid, M. Balden, J. W. Coenen, Loewenhoff, Th, A. Ito, A. Hasegawa, C. Hardie, M. Porton, and M. Gilbert. Baseline high heat flux and plasma facing materials for fusion. *Nucl. Fusion*, 57(9):092006, 2017.

[5] J. W. Coenen, Y. Mao, J. Almanstötterg, A. Calvo, S. Sistla, H. Gietl, B. Jasper, J. Riesch, M. Rieth, G.Pintsuk, and et al. Advanced materials for a damage resilient divertor concept for DEMO. *Fusion Eng. Des.*, 124(11):964–968, 2017.

[6] D. Maisonnier, I. Cook, P. Sardain, L. Boccaccini, E. Bogusch, K. Broden, L. Di Pace, R. Forrest, L. Giancarli, S. Hermsmeyer, and et al. The european power plant conceptual study. *Fusion Eng. Des.*, 75:1173–1179, 2005.

[7] F. Koch and H. Bolt. Self passivating W-based alloys as plasma facing material for nuclear fusion. *Phys. Scr.*, T128:100–105, 2007.

[8] A. Calvo, C.Garcia-Rosales, F. Koch, N. Ordas, I. Iturriza, H. Greuner, G. Pintsuk, and C. Sarbud. Manufacturing and testing of self-passivating tungsten alloys of different composition. *Nucl. Mater. Energy*, 9:422–429, 12 2016.

[9] T. Wegener, F. Klein, A. Litnovsky, M. Rasinski, J. Brinkmann, F. Koch, and Linsmeier, Ch. Development of yttrium-containing self-passivating tungsten alloys for future fusion power plants. *Nucl. Mater. Energy*, 9:394–398, 12 2016.

[10] J. Schmitz, A. Litnovsky, F. Klein, T. Wegener, X. Y. Tan, M.Rasinski, A. Mutzke, P.Hansen, A. Kreter, and A. Pospieszczyk et al. WCrY smart alloys as advanced plasma-facing materials - exposure to steady-state pure deuterium plasmas in PSI-2. *Nucl. Mater. Energy*, 15:220–225, 2018.

[11] F. Klein, T. Wegener, A. Litnovsky, M. Rasinski, X. Y. Tan, J. Gonzalez-Julian, J. Schmitz, M. Bram, J. W. Coenen, and Ch. Linsmeier. Oxidation resistance of bulk plasma-facing tungsten alloys. *Nucl. Mater. Energy*, 15:226–231, 2018.

[12] A. Litnovsky, T. Wegener, F. Klein, Linsmeier, Ch, M. Rasinski, A. Kreter, X.Y. Tan, J. Schmitz, J. W. Coenen, Y. Mao, and et al. New oxidation-resistant tungsten alloys for use in the nuclear fusion reactors. *Phys. Scr.*, 2017(T170):014012, 2017.

[13] S. Telu, R. Mitra, and S. K. Pabi. Effect of Y_2O_3 addition on oxidation behavior of W-Cr alloys. *Metall. Trans.*, 46(12):5909–5919, 2015.

[14] F. Koch, J. Brinkmann, S. Lindig, T. P. Mishra, and Linsmeier, Ch. Oxidation behaviour of silicon-free tungsten alloys for use as the first wall material. *Phys. Scr.*, 2011(T145):014019, 2011.

[15] T. Wegener, F. Klein, A. Litnovsky, M. Rasinski, J. Brinkmann, F. Koch, and Linsmeier, Ch. Development and analyses of self-passivating tungsten alloys for DEMO accidental conditions. *Fusion Eng. Des.*, 124:183–186, 2017.

[16] F. Klein, T. Wegener, A. Litnovsky, M. Rasinski, X. Y. Tan, J. Schmitz, Ch. Linsmeier, J. W. Coenen, H. Du, J. Mayer, and U. Breuer. On oxidation resistance mechanisms at 1273 K of tungsten-based alloys containing chromium and yttria. *Metals*, 8(7):488, 2018.

[17] J. R. Stephens. Effect of interstitial impurities on the low-temperature tensile properties of tungsten. *NASA Technical Note*, 1964.

[18] W. J. Quadakkers and J. Zurek In: J. A. Richardson et al (eds). *Shreir's Corrosion*, volume 1, chapter Oxidation in Steam and Steam/Hydrogen Environments, pages 407–456. Elsevier, 2010.

[19] E.T. Turkdogan. *Physical Chemistry of High Temperature Technology*. Academic Press, 1980.

Highlights

(max. 85 characters including spaces each)

- DEMO relevant conditions: bulk alloys in humid air above 1200 K

- Suppression of sublimation by more than one order of magnitude as compared to W

- Investigation on the applicability and its limits of advanced W-Cr-Y alloys

- Sublimation rate of 10^{-6} mg cm^{-2} s^{-1} of advanced W-alloys in humid air at 1273 K