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Smart tungsten alloys as first wall material for a future fusion power plant

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Abstract

Due to its low sputtering yield, excellent thermal conductivity and low tritium uptake tungsten is currently deemed as most promising plasma facing material (PFM) for future power plant DEMO. However, in case of an accident the coolant supply may be damaged. The air can get into contact with PFMs during the air ingress. According to modeling, the temperature of PFMs can rise up to 1200°C due to nuclear decay heat. At this temperature neutron-activated tungsten forms the volatile radioactive oxide which can be mobilized into the atmosphere. Therefore, oxidation of tungsten must be avoided.

Self-passivating “smart” alloys are being developed to suppress tungsten oxidation. Smart alloys can adjust their properties to the environment. During plasma operation the preferential sputtering of lighter alloying elements will leave a pure tungsten surface facing the plasma. During an accident the alloying elements in the bulk are forming stable oxides thus protecting tungsten from mobilization.

The isothermal oxidation of thin film alloys produced by magnetron sputtering was carried out at 1000°C in the atmosphere containing 80 vol.% of Ar and 20 vol. % of O₂. Oxidation resulted in the dramatic 3.0×10^6 fold reduction of the oxidation rate as compared to that of pure tungsten.

Manufacture of bulk materials based on experience gained from the thin films is crucial. Bulk W-Cr-Ti samples were produced at CEIT (Spain) from mechanically alloyed powders treated by hot isostatic pressing at 1200°C at the pressure of 150 MPa.

Smart alloys and pure tungsten samples were exposed to the steady-state deuterium plasma under identical conditions in the linear plasma device PSI 2 at FZJ. The temperature of the samples was ~700°C, the energy of impinging ions was 210 eV matching well the conditions expected at the first wall of DEMO. The total fluence was 1.3×10^{26} ion/m². Weight loss measurements demonstrated similar mass decrease of smart alloys and of pure tungsten samples after exposure implying that the sputtering rate of smart alloy is mostly defined by sputtering of its tungsten matrix. Plasma tests are followed by the oxidation of exposed samples comprising the first complete performance test of smart alloys in DEMO-relevant conditions.

Introduction and motivation

Tungsten is among prime candidate materials to be used for plasma-facing components in the future fusion power plant. Among the advantages of tungsten for fusion applications are: low sputtering yield by plasma ions, high thermal conductivity at elevated temperature, low retention of radioactive tritium and high melting temperatures. At the same time, the construction of the future power plant will raise significantly the limits and requirements which are imposed on the plasma-facing materials. In addition to already harsh plasma conditions expected in next fusion experiments the accumulated neutron fluence is expected to be orders of magnitude higher bringing several physical and engineering challenges including the high level of the nuclear decay heat at the PFC. The expected stationary or quasi-stationary operation will extremely increase the plasma particle fluxes towards the plasma-facing components. According to the recent investigations [1], none of existing materials will withstand the combination of particle and heat loads and intensive neutron irradiation.

In particular, in case of Loss-of-Coolant-Accident (LOCA) with an air ingress, the temperature of non-cooled tungsten components may rise till 1200°C and remain at such a level for several weeks [2]. Activated tungsten forms at these temperatures the radioactive oxide which will be mobilized into atmosphere at a rate of 1 -100 kg/h. This is an unacceptable value.

In order to counteract the undesirable oxidation of tungsten and to keep its advantageous features the new advanced, so-called “smart” alloys were introduced. Smart alloys are supposed to adjust their properties to the environment. During regular plasma operation of power plant, preferential sputtering of alloying elements will leave almost pure tungsten surface turned to plasma. In case of an accident, such a thin tungsten – rich surface of ~ 10 nm will oxidize and will be mobilized into environment. Alloying elements in the bulk of the smart alloy will however, remain. These alloying elements will create their own dense oxide layers protecting tungsten matrix from oxidation and evaporation. Smart alloys provide an essential element of the so-called intrinsic safety of the future power plant. The schematic of operation of smart alloy is provided in Fig.1.

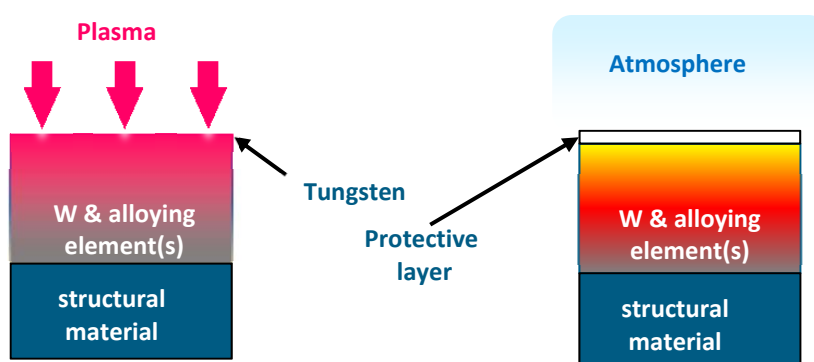


Figure 1. The scheme of operation of smart alloys during the regular plasma operation and under accidental conditions.

There are several essential limitations imposed on alloying elements for the fusion applications. Alloying elements need to possess low activity, ability to form stable oxides and low volume increase during oxidation. Among remaining alloying elements are Cr, Si, Vn, Ti and Y.

Investigations of self-passivating tungsten-based smart alloys

There is an essential research on self-passivating smart alloys [3-7]. Investigations made on binary and ternary systems led to discarding Si-containing systems [5]. The present investigations are focused on ternary chromium-containing smart alloys. The present paper is focused on newest developments in advanced smart alloys made and studied at the Forschungszentrum Jülich GmbH (FZJ) and provided by the partner institute CEIT, Spain.

The research on smart alloys comprise the dedicated studies on the near-to-ideal, homogenous at atomistic scale, well-defined thin (3-7 μm) films produced by magnetron sputtering. Such thin films are being used for the understanding of fundamentals of the oxidation and for initial evaluation of the new smart alloys. At FZJ, a multi-electrode magnetron system from PREVAC was used for production of thin-film alloys. Three targets made from tungsten and alloying elements are depositing material onto a rotating table with samples.

The essential features of smart alloys are their resistance to plasma sputtering and the suppression of the oxidation. Suppressed oxidation most obviously manifests itself via low mass gain in the course of the controlled oxidation. Such measurements are made using the symmetrical double-oven thermogravimetric (TGA) system TAG 16 from Setaram. The system

is also equipped with the steam generator allowing performing experiments in humid atmosphere. The TGA system is located in the new just commissioned ThermoLab at the FZJ. Mass change was monitored using the high-resolution microbalance. The surface roughness was monitored using stylus profiler Dektak 6M from Bruker. Visual observations were made using the inverted microscope Carl Zeiss Axio Observer Z1m. All mentioned equipment is located in the MirrorLab [8] at FZJ.

In addition, the crystallographic structure, phases of constituents can be investigated using X-Ray Diffraction (XRD) system from Bruker. Elemental composition of matrix and alloying elements along the depth of the probe was investigated using Secondary-Ion-Mass-Spectrometry ION-ToF IV system. Elemental composition, morphology, homogeneity was investigated using Carl Zeiss CrossBeam XB 540 a combined scanning electron microscope (SEM) and focused ion beam (FIB) system. The CrossBeam is equipped with electron back-scattering system (EBSD), energy-dispersive X-ray analysis (EDX), transmission electron module (STEM), plasma cleaner and the vacuum gate system.

Yttrium-containing thin film smart alloys

Good oxidation resistance was observing when yttrium was introduced as a so-called active element in the alloy. Yttrium is primarily known from its successful application in the steel industry. Adding yttrium to alloy system may:

- Introduce pegs at the interface between the alloy and the oxide scale [9, 10]. Pegs are acting as a connection between the oxide and the alloy which may increase the adherence of the oxide scale to the alloy system [9, 10, 11]
- Alter transport mechanisms through the oxides. Yttrium is usually segregated to the grain boundaries [12, 13] where the transport occurs. The oxygen scale grows from the alloy and yttrium acts as a vacancy sink to suppress the formation of voids and pores at the interface [14, 9].
- Due to its chemical reactivity, yttrium is actively bonding the impurities preventing them from entering the oxide scale. The presence of impurities in the oxide may otherwise destabilize the oxide layer [14].

Yttrium is known for its ability to limit the grain size growth [14] and to decrease the growth rate of an oxide scale [14]. This element is shown not to have cation transport moreover, it suppresses the cation transport of the other elements, leading e.g. to a decrease of the growth stresses and improved adherence, when Y is present in small amounts [9, 12].

Yttrium-containing films produced at FZJ featured very good homogeneity. Chromium fraction contributed to apr. 8 to 12 weight %, an amount of Y was about less than 1 wt. % of the alloy. The results of the comparative oxidation study of pure tungsten and smart alloys are provided in Fig. 2.

The oxidation rate of W-Cr-Y alloy, characterized by a mass increase is significantly lower than that of any shown by W-Cr and W-Cr-Ti systems. The microscope and FIB investigations revealed the formation of the thin and dense chromium oxide protecting tungsten from oxidation and subsequent evaporation. The respective FIB scan is provided in Figure 3. Obviously, the formation of such a dense protective layer is responsible for the suppressed oxidation.

The series of TEM investigations were made on thin lamella cut from the upper part of the oxidized thin-film smart alloy. The EDX mappings of the constituent elements are shown in Figure 4. The created protective Cr_2O_3 oxide contains no trace of tungsten. What is more interesting however, is the distribution of Y. During investigations two pronounced distributions

of Y were detected. Firstly, there are some pre-cursors of the formation of the nucleation sites which is agreement with the expected distribution of Y.

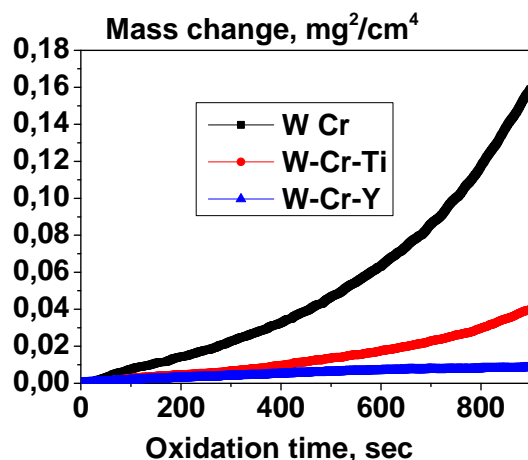


Figure 2. Oxidation of different smart alloys in 80 vol.%Ar + 20% vol.% O₂ at 1 bar and the temperature of 1000°C

At the same time, there is obviously homogenous distribution of yttrium in the bulk of the sample. Whether the nucleation sites are responsible for the good passivation or the homogenous distributions and hence immediate availability of yttrium in the bulk of the sample are playing the decisive role in the passivation - remains an open question. It is supposed that the observed two different distributions of Y may play the decisive role in understanding of the oxidation behavior of the bulk smart alloys.

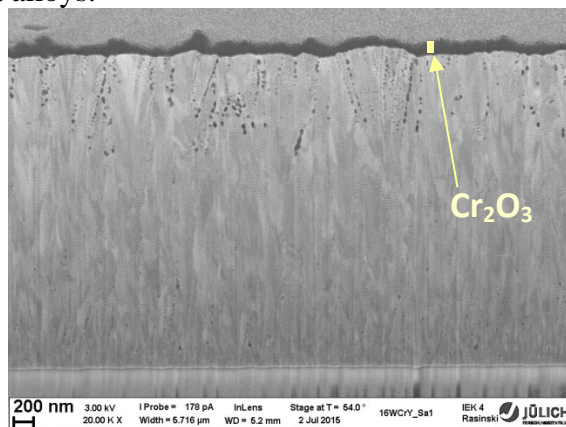


Figure 3. FIB cut of W-Cr-Y thin film smart alloy after 10 minutes of oxidation at 1 bar in 80 vol.%Ar + 20% vol.% O₂ at 1000°C

Knowledge obtained after studies of the model thin-film systems was afterwards applied for production of the bulk smart alloys. Presently, the manufacturing route towards the bulk smart alloy comprises several steps. On the first step, mechanical alloying of initial elemental powders is made using the planetary milling system. The alloyed powder underwent hot isostatic pressing at 1200°C at the pressure of 150 MPa. Manufactured bulk material featured nanocrystalline tungsten grains of about 90-110 nm and contained 10 wt.% of Cr, 2 wt.% of Ti and the rest of W.

Details of the manufacturing process and the initial characterization of manufactured materials are provided in [6].

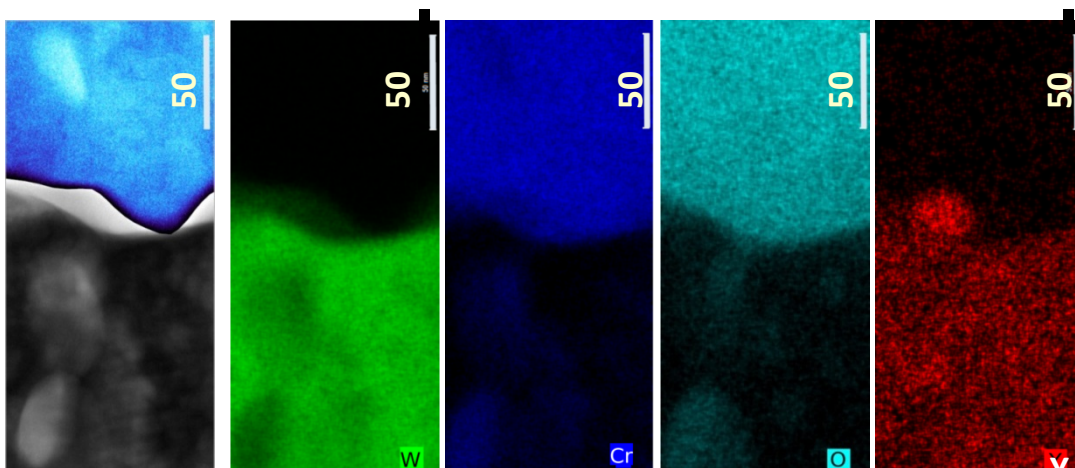


Figure 4. Color maps of the EDX measurements made on the TEM lamella, at the interface between smart alloy and the protective oxide layer.

Plasma exposure of smart alloys and pure tungsten samples

In addition to the suppressed oxidation, new materials need to be qualified under plasma exposure. The first results of such a plasma exposure along with the subsequent oxidation of exposed tungsten and smart alloy samples are reported in this paper.

The W-Cr-Ti smart alloy samples were produced at CEIT (Spain) from elemental tungsten, chromium and titanium powders. The alloyed powder underwent hot isostatic pressing. Manufactured bulk material contained 10 wt.% of Cr, 2 wt.% of Ti and the rest of W. Tungsten and smart alloy samples were characterized before the plasma exposure.

Special markers were made with an ion beam on the side surface of each FIB crater. The distance between the two neighboring markers corresponded to 1 μ m. The markers were used for direct measurements of the material sputtered during plasma exposure.

The pre-characterized samples were exposed to steady-state deuterium plasma in linear plasma device PSI 2 [10]. During exposure plasma parameters were monitored using the moveable Langmuir probe. The measured electron temperature was 30-35 eV, the plasma density was $N_e \sim 7 \times 10^{11}$ ion/cm³. The measured ion flux was 1×10^{18} D/(cm²×s). Samples were biased at -250 V. The temperature of the samples was controlled via thermocouple mounted behind the sample and using the infrared FLIR camera. During the exposure the temperature of samples was ranging from 576°C to 715°C. The total duration of the exposure was 3.6 hours, the total accumulated fluence was estimated to be 1.3×10^{26} D/cm².

After the exposure the samples were weighed. For exposed tungsten sample W1 a mass loss of 1000 μ g was measured, tungsten sample W2 exhibited the mass loss of 1150 μ g as provided in the table 1. The decrease of the mass loss of exposed smart alloy SA1 sample was measured to be 1240 μ g. The attained sputtering yield of tungsten of 2.4×10^{-4} at/ion corresponds well to the experimental data provided in [11] however, it is a bit higher than that expected from theory [12, 13]. The reason for more effective erosion in plasma of PSI 2 linear device may be attributed to the small 0.1% fraction of oxygen in plasma. The calculated removal of material by sputtering

from the mass loss measurements was estimated to be: 500 nm for tungsten and about 800 nm for a smart alloy.

Table 1. Characteristics of tungsten and smart alloy samples during and after plasma exposure

Sample	Temperature during exposure, °C	Weight loss during exposure, µg
W1	702	1000
W2	665	1150
SA1	715	1240
SA2	576	n.a.

The sputtered depth was measured directly using the craters pre-marked with the focused ion beam as described earlier. The removed amount of material due to sputtering from the weight loss measurements was compared for tungsten with the value measured using FIB crater. The expected loss of tungsten was 500 nm, whereas the direct measurements showed 560 nm outlining the perfect correlation between weight loss and direct measurements of sputtered material. The measured material removal from the smart alloy sample was about 900 nm which is in a very good correlation with the weight loss measurements. The evidence of a preferential sputtering of alloying elements was provided by the dedicated SIMS measurements made on all samples.

Effect of plasma exposure on oxidation resistance of smart alloys

In order to study the effect of plasma exposure on oxidation properties of smart alloys, series of thermo-oxidation studies were performed after plasma exposure. During the thermo-oxidation measurements, the samples were placed in synthetic air atmosphere containing 80 vol. % N₂ and 20 vol. % O₂ at 1 atmosphere and oxidized isothermally at the temperature 1000°C for ten hours. The choice of temperature corresponds to the expected value during the accident on the fusion power plant [2]. The samples were exposed under identical conditions. Three samples were chosen for thermo-oxidation tests: pure tungsten sample, manufactured and rolled according to the ITER specifications, smart alloy which were never exposed to plasma and smart alloy after plasma exposure.

The resulting dependencies are presented in Figure 5 as the mass gain over time. Pure tungsten sample is remarkable for the by far highest linear oxidation rate of 6×10^{-3} mg/(cm²×s). Smart alloys feature the significant suppression of oxidation: the measured oxidation rate of 2×10^{-3} mg/(cm²×s) was detected for W-Cr-Ti smart alloy systems both exposed and non-exposed to plasma. The same oxidation behavior of smart alloys confirms our expectations that plasma exposure does not have any negative effect on oxidation advantages of smart alloys.

At the same time, the mass gain during the oxidation is linearly proportional to time for all studied systems. This result means that the suppression of oxidation in the studied samples is not accompanied with self-passivation. Should this happen, the oxidation would follow diffusion-driven square root dependence on time. This finding outlines explicitly the need in future optimization of smart alloys despite of significant suppression of tungsten oxidation already detected in the course of present studies.

Summary and outlook

New advanced materials are required for the safe and reliable operation of the future fusion power plant. Among these materials, self-passivating tungsten-based smart alloys are aimed at

getting the acceptably low plasma sputtering rate during regular plasma operation and suppressed oxidation of tungsten under accidental conditions.

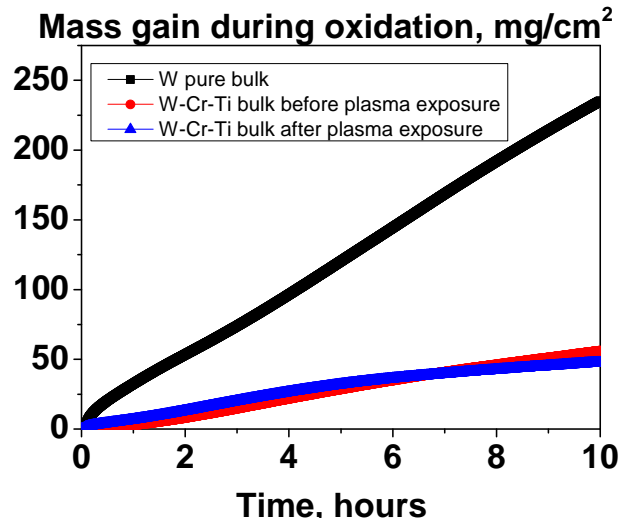


Figure 5. Mass gain caused by the oxidation of the pure tungsten and W-Cr-Ti smart alloys.

Very promising results were reached with the model smart alloy thin films containing yttrium. Adding the small amount of < 1 wt.% of yttrium to the tungsten-chromium alloy was capable to stabilize the protective Cr₂O₃ layer, to make it more compact and dense and decrease the oxygen diffusion into alloy bulk. The remarkable oxidation rates of 3×10^{-6} mg²/cm⁴ per second were attained, constituting the more than 10⁵-fold difference to that of pure tungsten. Tungsten-chromium-yttrium systems are also featuring the most stable passivation behavior among all studied smart alloy systems.

First direct comparative plasma test of advanced smart tungsten-based alloys and pure tungsten samples was made under conditions expected at the first wall in DEMO. Exposed under identical plasma conditions, tungsten and smart alloy samples demonstrated similar sputtering under plasma ion bombardment. The expected preferential sputtering of alloying elements during the plasma exposure of smart alloys was confirmed experimentally. Controlled oxidation of smart alloys did not reveal any negative effect of plasma exposure on the suppressed oxidation.

New yttrium-containing tungsten smart alloys became available recently. The new W-Cr-Y systems feature more effective long-term suppression of tungsten oxidation coupled with better long-term stability of protective layers. The plasma tests of these innovative new smart alloys are in preparation. The sputtering of new smart alloys by plasma, corresponding surface changes and the deuterium retention in the exposed samples is in focus of future research. The combined full working cycle test including plasma and oxidation testing of new systems is of prime importance. Future studies will be carried out to optimize the overall performance of smart alloys including thermo-mechanical properties of these materials such as: thermal conductivity, hardness and ductile-to-brittle transition temperature.

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