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Smart first wall materials for intrinsic safety of a future power plant

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The first wall armor of a DEMOnstration fusion power plant (DEMO) is planned to be built from tungsten. However, in case of loss-of-coolant accident with air ingress, the temperature of the first wall may exceed 1000°C due to nuclear decay heat. At such temperatures, tungsten forms volatile radioactive oxides, which may be mobilized into the environment at a rate of 10-600 kg per hour.
New "smart" tungsten alloys adjust their properties to the environment: during the plasma operation, preferential sputtering will form almost pure tungsten surface facing the plasma. In case of an accident, the remaining alloying elements form a protective layer, preventing tungsten mobilization.
The new smart alloys contain tungsten (W), chromium (Cr) and yttrium (Y). The first bulk smart alloys produced using field-assisted sintering technique, revealed excellent oxidation resistance for a timescale of 10-20 hours. W-Cr-Y systems underwent combined plasma and oxidation test. During plasma exposure, smart alloys demonstrated nearly the same mass loss as the reference pure tungsten samples. Subsequent oxidation confirmed superior oxidation resistance of new alloys compared to the former W-Cr-Ti systems.
Experiments attaining oxidation times and plasma fluence required for DEMO, are started. First results show necessity in further improvement of W-Cr-Y alloys.

Keywords: DEMO intrinsic safety, self-passivating smart alloys, accidental conditions, suppressed oxidation, resistance to sputtering

1. Introduction: DEMO fusion power plant

A future fusion power plant, will impose the highest requirements for reliability and safety. Assessment studies helped to identify potential risks. Among those is the so-called accidental scenario, comprising the loss-of-coolant-accident (LOCA) with an air ingress leading to a direct contact of the plasma-facing components with air.

The choice of plasma-facing components represents a challenging task. Due to its high thermal conductivity, low sputtering by plasma, high melting point and relatively low activation, tungsten is presently envisaged as a prime candidate plasma-facing material for a future power plant.

However, the use of pure tungsten implies a potential severe problem with power plant safety. Under accidental conditions described above, the temperature of tungsten PFCS will rise up to 1200°C and above due to nuclear decay heat [1] in the absence of a coolant. Such a high temperature remains for months after an accident. Under these conditions, tungsten oxidizes in the contact with air. The formed tungsten oxide WO_3 is volatile, it sublimates as an aerosol into the environment with the rate of 10-600 kg/hour yielding to a massive release of the radioactive material. Such a release must be avoided.

Given the present experience with major nuclear accidents in Fukushima and Chernobyl, it must be assumed that there will be difficulties with logistics, electricity and manpower at least during the first days after an accident. Under such conditions, intrinsic, "built-in" safety plays an increasingly important role.

2. Smart alloys

New advanced tungsten-based self-passivating, so-called smart alloys are under development as a intrinsic safety measure for future fusion power plant. The general concept of a smart alloy is graphically represented in [2, 3]. This advanced material must adjust its properties to the environment. During regular plasma operation, plasma ions and energetic neutrals will preferentially sputter lighter alloying elements, leaving almost pure W surface facing the plasma. During accidental conditions, alloying elements stored intact in the bulk of a smart alloy will cause the prompt oxidation and form their dense oxide layer, effectively protecting tungsten oxide from a sublimation.

Significant progress has been made in the recent years in development of smart alloys [4-6]. Currently, the most advanced smart alloy system contains chromium (Cr) as a passivating element and

a small fraction of yttrium (Y), acting as an active element. Yttrium has a number of positive effects on both stability and durability of the smart alloy system, which are briefly summarized in [3]. Recently, the bulk smart alloy systems of DEMO-relevant sizes became available. The production of bulk systems consists from two phases:

1. Mechanical alloying of elementary W, Cr and Y powders. As the result of mechanical alloying, the solid solution of W and Cr is formed. Yttrium is present in the form of yttria in the final alloyed powder.
2. Powder-metallurgical route. The alloyed powder undergoes HIP process [7, 8] at temperatures of 1200ºC for several hours. Recently, the Field-Assisted Sintering Technology (FAST) was applied for manufacturing of bulk smart alloys. FAST features extremely short times (minutes) needed for the sintering and very homogenous W, Cr and Y distributions.

In present paper, smart alloys produced with FAST are described. The best FAST samples, produced so far, featured the miniature W-Cr alloy sub-micrograins with a size of 100-200 nm, surrounded by the 15-30 nm yttria nanoparticles. Such a homogeneity allowed the newly developed smart alloy bulk system to supersede model magnetron-deposited smart alloy thin films on their oxidation resistance [9].

The next step in the development of the smart alloy system is a performance test. Since smart alloys are the candidate plasma-facing first wall materials for DEMO, the performance test comprises the exposure of smart alloys in steady-state plasmas under DEMO relevant conditions, followed by the oxidation of plasma-exposed samples, thus addressing accidental conditions in a power plant.

2.1 First performance tests of W-Cr-Y alloys

The first plasma tests of new yttrium – containing smart alloys were made in March 2017. The arrangement of the experiment was very similar for the first complete performance tests of former W-Cr-Ti systems [10]. First results of the experiment are presented in [11].

The bulk samples were manufactured from the alloyed W-Cr-Y powder following the procedure described in [9]. The alloyed powder underwent the FAST with the following parameters:

1. Applied pressure: 50 MPa
2. Temperature ramp: 200ºC/min
3. Maximum attained temperature: 1550ºC
4. Sintering holding time: 1 minute

FAST was made with FAST/SPS facility FCT-HDP5 from FCT-Systeme. The resulting samples were cut from the ingot using spark erosion and subsequently ground manually to the surface roughness R_a~30 nm.

The manufactured samples underwent a thorough characterization before and after exposure. The integral mass change was monitored with the Sartorius MSA225P microbalance with a resolution of 10 µg. Amount of removed material was estimated according to weight loss and independently using Focused Ion Beam (FIB) system. Special craters were made on all samples using FIB. These craters had markers made with an ion beam, every 1 µm in depth of the crater. The amount of removed material was inferred directly by inspecting the markers after exposure.

Surface morphology was monitored using the scanning electron microscope (SEM). The combined SEM-FIB system Carl Zeiss CrossBeam XB540 equipped with Energy Dispersive X-ray analysis system (EDX) was used for investigations. Sample roughness was measured with stylus profiler Dektak 6M from Veeco/Bruker. Depth distribution of tungsten and alloying elements was investigated with Secondary Ion Mass-Spectrometry (SIMS), ION ToF SIMS IV.

Smart alloy and pure tungsten reference samples were installed in the sample holder at the same radial position in order to ensure the same plasma conditions for all exposed samples. Exposure was performed in the steady-state deuterium plasma in the PSI 2 linear plasma device [12]. Plasma parameters were monitored using the moveable Langmuir probe. Electron temperature was Te~6-8 eV depending on radial position. With an active biasing applied to the samples, the energy of impinging ions was ~ 220 eV. The samples were actively heated to the temperature of 620ºC-650ºC. The temperature was monitored with the thermocouple installed on the backside of one of the samples. The plasma-exposed area of all samples was 1cm^2. Ion energy and the temperature during exposure provided a conservative estimate of the environment expected in DEMO [13]. The total exposure duration was four hours 36 minutes. The accumulated fluence was 1×10^{22} ion/cm^2.

The results of the exposure are briefly summarized in table 1. Very similar mass loss was detected both for pure tungsten and for smart alloy samples, underlining the similarity of sputtering of these materials under given conditions. At the same time, the volumetric loss of smart alloy was more significant than that of pure tungsten, as expected for a given elemental composition of the alloy. The surface roughness increased after sputtering, as expected. Generally, the first exposure demonstrated a good resistance of smart alloys to the stationary deuterium plasma under experimental conditions. The plasma test was followed by the controlled

oxidation of the plasma-exposed sample. The oxidizing exposure was conducted at temperature of 1000°C in the gas mixture containing 20 vol.% O_2 and 80 vol.% Ar. The resulting dependencies demonstrate much better oxidation resistance of new W-Cr-Y alloys than former W-Cr-Ti systems after plasma exposure.

Table 1. Exposure parameters and characteristics of pure tungsten and smart alloy samples

Exposure parameters	Ion energy, eV	Fluence, ion/cm^2	Duration of exposure, h	Sample temperature, C
	220	1.0x10^{22}	3 h 16‘	620
Sample	Mass loss [μg]	Eroded material, nm	$R_{a,\ before}$ [nm]	$R_{a\ ,\ after}$ [nm]
W1	1200±10	460	30±7	141 ±55
W2	1093±10	440	24±8	52± 49
SA1	1287±10	860	22±5	46±25
SA2	1223±10	870	24±9	47±32

Such a difference is most probably, to be attributed due to a different geometry (and hence different oxidizing flow) of plasma-exposed and non-exposed samples. In addition, the plasma-exposed sample likely contained areas affected by spark erosion, which were impossible to remove and which have possibly affected the oxidation.

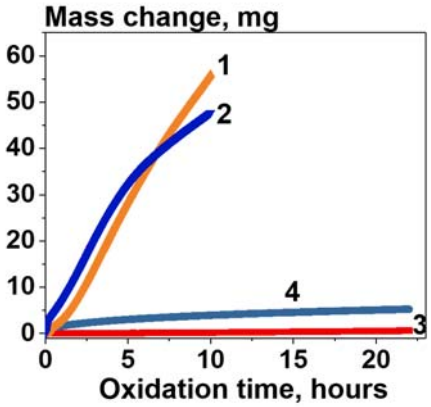

Figure 1. Impact of plasma exposure on oxidation characteristics of bulk W-Cr-Ti and W-Cr-Y smart alloys, represented as a dependence of mass change on time of 1) W-Cr-Ti alloy before plasma exposure, 2) W-Cr-Ti alloy after plasma exposure, 3) W-Cr-Y alloy before plasma exposure and 4) W-Cr-Y alloy after plasma exposure.

2.2 Next step: lifetime of advanced smart alloys in DEMO

As can be seen from investigations above, bulk smart alloys already performed very well on the time scale of 10-20 hours. This means, that the self-passivating smart alloy systems already reached the next level and are now capable of addressing the topics of their direct application in DEMO for their entire lifetime in the power plant. Lifetime investigations at their present scope, mean:

1. Studies of plasma performance at particle fluence corresponding to the first wall of DEMO during the entire lifetime of the wall
2. Studies of oxidation behavior on the time-scale, exceeding the envisaged accident scenario for DEMO of ~ 60 days.

A first such a long-term oxidation exposure was made recently. A W-Cr-Y smart alloy was exposed at 1000°C in a gas mixture of 20 at.% of O_2 and 80 at.% of Argon for more than 480 hours. The evolution of mass with a time is presented in Fig.2.

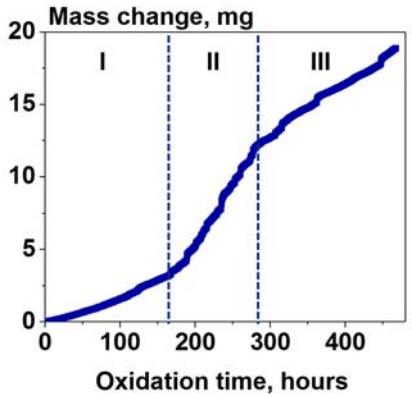

Figure 2. Mass change with a time of the bulk W-Cr-Y in the course of long-term oxidation. Oxidation performed in the gas mixture containing 80 vol.% of Ar and 20 vol. % of O_2 at 1000°C performed at the pressure of 1 bar.

As can be seen from the figure, the passivation-like behavior (phase I) breaks after about 160 hours of oxidation. The following phase II is remarkable by its instable mass change. The step-like increases may be attributed to the breakaway oxidation. The most probable mechanism of breakaway oxidation is the transport of W through the protective layer followed by the oxidation of W accompanied with the extreme volume increase (Pilling Bedworth ratio of volumes V: V_{oxide}/V_{metal} =3.39 [14]). Even more surprising, is a

relatively calm phase III which steps in after about 280 hours of oxidation. No explanation for such a "self-healing" behavior is found so far and the long-term oxidation behavior is currently in the focus of investigations.

Dedicated pilot studies already revealed several failures in the alloy protection. The corresponding FIB cross-section is shown in Fig 3. As can be noticed, there is already the destruction of homogeneity of the protective layer and a presence of the mixed W-Cr-O oxides at the surface. Certainly, more efforts must be spent on ensuring the long-term passivation of smart alloys.

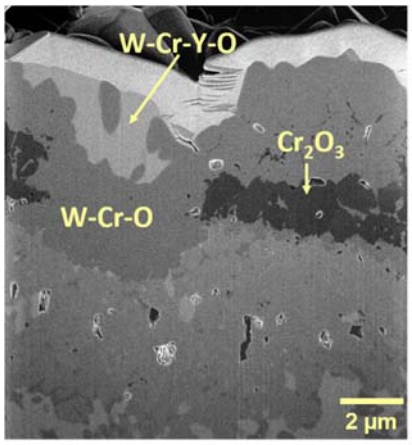

Figure 3. A Cross-section of the FAST bulk smart alloy W-Cr-Y sample after 467 hours of oxidation in the gas mixture containing 80 vol.% of Ar and 20 vol. % of O_2 at 1000°C performed at the pressure of 1 bar.

In reality, in case of an accident, the probability is rather small, that smart alloys undergo oxidation under dry air conditions. Therefore, a passivation in the humid atmosphere environment is crucial for a success of smart alloys. The dedicated studies are now started using the TAG 16 TGA system along with WetSys steam generator. The first measurements were made on thin films. The respective dependencies are shown in Fig. 4. The initial parabolic dependence on time was violated at least twice where the mass increase stopped or even reverted. Those two time intervals are marked with arrows in the Fig.4.

The observed mass decrease is most probably, due to sublimation of alloy material– an extremely dangerous event in a power plant. The reasons for such an increased reactivity of smart alloys in the humid air environment are in different chemical channels of the oxidation reaction. Some of these channels are intrinsic for humid environment e.g. transport of hydroxide ions (OH^-). In addition, an initial partial pressure of oxygen during the exposure in humid air is much larger than that in dry atmosphere. The detailed study is reported in [15] where the dominant role of W in the sublimation of the smart alloy was demonstrated

Till now, the efforts are concentrated on suppression of oxidation. It is however, not an oxidation what causes radiological hazard. Namely, it is a sublimation of oxide, which is truly responsible for a release of oxidized radioactive materials. The measurements of sublimation are however, very time taking and challenging. The initial estimates are provided in the next paragraph.

The first attempts to measure the sublimation directly were undertaken with dedicated samples. The exposure took place at the most extreme conditions ever envisaged for smart alloys: temperature of oxidation was set to 1200°C, the humid air had 70% relative humidity. The samples were first oxidized to attain the regime of net sublimation. The complete oxidation of the W-Cr-Y smart alloy happened within 4 hours. The measured mass loss due to sublimation were apr. 4 mg. The experimentally obtained sublimation rates are as high as 1.5×10^{-3} mg/(cm^2×s) at aforementioned conditions.

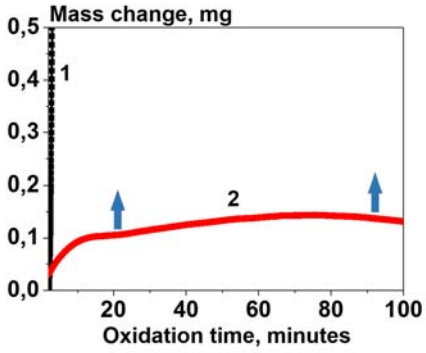

Figure 4. Mass change in the course of the oxidation in the atmosphere containing 80 vol.% of N_2 + 20 vol.% O_2 at 70% relative humidity at 1000°C fed at 1 bar into the reaction volume for 1) pure thin film tungsten sample and 2) thin film W-Cr-Y smart alloy. Arrows show the time slices with probable sublimation.

An extrapolation of the observed sublimation rates for DEMO power plant was performed with the following conditions:

- An area of the first wall: 1000 m^2
- Temperature after accident: 1200°C
- Thickness of the first wall cladding: 2 mm

The activation rates can be obtained e.g. from [16]. The corresponding amount of released material is about 38 tons and the resulting immediate activity 1.9×10^{18} Bq is expected to be induced according to the linear extrapolation of the elemental content multiplied by corresponding activation from tungsten and alloying elements [16]. This value can be compared e.g. with the total activity released during a major nuclear accident in Fukushima, which is 5.2×10^{17} Bq [17]. This an inacceptable value, clearly underlining the necessity in further optimization of smart alloys.

3. Summary and outlook

Recent studies show an impressive progress in research and development of the advanced tungsten-based smart alloy systems. During the last year, a FAST technique was applied for manufacturing of the bulk W-Cr-Y alloys for the first time. Produced samples already

possess high homogeneity and, an excellent oxidation resistance on a timescale of 10-20 hours. Such a suppression of oxidation is more intensive than that from the reference thin film system. First plasma test revealed clearly superior performance of W-Cr-Y alloys in comparison to the former W-Cr-Ti smart alloy systems under DEMO-relevant plasma conditions.

These studies allowed to pursue the next step of the material qualification by making more challenging exposures of smart alloys. These exposures are aimed at studying the entire lifetime of these materials in DEMO including both plasma operation and an accident.

The first such studies however, clearly indicated a significant challenge on the way of robust material with a long lifetime. The long 20-day oxidation revealed a transformation of the protective coating to the mixed W-Cr-O mixed oxide layer, possibly leading to the release of tungsten. Detailed studies demonstrated degradation of protecting Cr_2O_3 coating. Remarkably, after 280 hours of oxidation, some recovery of oxidation resistance was noticed.

The first tests performed with the thin film smart alloys demonstrated detrimental performance during the exposure in humid air atmosphere – a next step towards addressing a realistic situation in DEMO. High mobilization rates call for further improvement of smart alloys.

Future studies will be devoted to further improvement of FAST technology of manufacturing of bulk samples in order to provide even higher homogeneity of alloying element distribution along with the higher endurance of manufactured samples. With new samples we plan to improve a long-term oxidation resistance of smart alloys including suppression of sublimation in humid atmosphere. Here, the ultimate target is to suppress or to postpone significantly the onset of the tungsten sublimation in the timescale of months. This will directly address the expected performance under most conservative conditions envisaged for DEMO.

New high fluence plasma exposures are envisaged, aiming at reaching the fluence corresponding to one year of DEMO operation. The resulting sputtering rates and the developed surface roughness, which largely governs an oxidation resistance, are expected to provide a valuable input for DEMO studies.

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