Nuclear Materials and Energy 000 (2016) 1–8

Contents lists available at ScienceDirect

Nuclear Materials and Energy

journal homepage: www.elsevier.com/locate/nme

# Manufacturing and testing of self-passivating tungsten alloys of different composition

A. Calvo[a], C. García-Rosales[a,*], F. Koch[b], N. Ordás[a], I. Iturriza[a], H. Greuner[b], G. Pintsuk[c], C. Sarbu[d]

[a] Ceit-IK4 Technology Center and Tecnun (University of Navarra), E-20018 San Sebastián, Spain
[b] Max-Planck-Institut für Plasmaphysik, D-85748 Garching, Germany
[c] Forschungszentrum Jülich GmbH, D-52425 Jülich, Germany
[d] National Institute of Materials Physics, R-077125 Magurele-Bucharest, Romania

ARTICLE INFO

*Article history:*
Available online xxx

*Keywords:*
Tungsten alloys
Oxidation resistance
Armour material
Mechanical alloying
HIP

ABSTRACT

Self-passivating tungsten based alloys for the first wall armour of future fusion reactors are expected to provide a major safety advantage compared to pure tungsten in case of a loss of coolant accident with simultaneous air ingress, due to the formation of a stable protective scale at high temperatures in presence of oxygen which prevents the formation of volatile and radioactive $WO_3$.

Bulk W-15Cr, W-10Cr-2Ti and W-12Cr-0.5Y alloys were manufactured by mechanical alloying followed by can encapsulation and HIP. This route resulted in fully dense materials with nano-structured grains. The ability of Ti and especially of Y to inhibit grain growth was observed in the W-10Cr-2Ti and W-12Cr-0.5Y alloys. Besides, Y formed Y-rich oxide nano-precipitates at the grain boundaries, and is thus expected to improve the mechanical behaviour of the Y-containing alloy. Isothermal oxidation tests at 800 °C (1073 K) and oxidation tests under accident-like conditions revealed that the W-12Cr-0.5Y alloy exhibits the best oxidation behaviour of all alloys, especially in the accident-like scenario. Preliminary HHF tests performed at GLADIS indicated that the W-10Cr-2Ti alloy is able to withstand power densities of 2 MW/m$^2$ without significant damage of the bulk structure. Thermo-shock tests at JUDITH-1 to simulate mitigated disruptions resulted in chipping of part of the surface of the as-HIPed W-10Cr-2Ti alloy. An additional thermal treatment at 1600 °C (1873 K) improves the thermo-shock resistance of the W-10Cr-2Ti alloy since only crack formation is observed.



## 1. Introduction

In future fusion reactors such as DEMO, a potential loss-of-coolant accident with simultaneous air ingress into the vacuum vessel would involve temperatures of the in-vessel components above 1000°C (1273 K) because of the decay heat [1]. Under this situation, the use of pure tungsten, presently planned for the blanket protecting first wall armour [2], represents an important safety issue due to its high oxidation rate at high temperatures, which would lead to full oxidation of the armour layer. Since tungsten oxide is rather volatile at the involved temperatures, part of the tungsten would be mobilized with the consequent release of highly activated species [3]. A possible way to avoid the risk of radioactive release during such a scenario would be the addition of oxide forming alloying elements to tungsten, resulting in the formation of a stable protective oxide scale at high temperatures in presence of oxygen. During normal operation, the surface of this self-passivating alloy will consist of pure tungsten, owing to preferential sputtering of the alloying elements.

In previous works [4-6], different bulk tungsten alloys of the systems W-Cr-Si and W-Cr-Ti were manufactured by mechanical alloying (MA) and densification by Hot Isostatic Pressing (HIP). The addition of Cr and Si or Ti as alloying elements resulted in a reduction of the oxidation rate by several orders of magnitude at temperatures up to 1000°C (1273 K) compared to pure tungsten, due to the growth of a protective oxide layer [4,7-9]. Nevertheless, Si tends to form brittle intermetallics with detrimental effect on the workability of the alloys and Ti contributes to enhance tritium retention [10]. Both reasons have motivated the search for alternative systems avoiding Si [6,8] and Ti as alloying elements. Binary W-Cr alloys represent a feasible alternative; such alloys have

* Corresponding autor.
*E-mail address:* cgrosales@ceit.es (C. García-Rosales).

http://dx.doi.org/10.1016/j.nme.2016.06.002

been subject to several investigations aiming at improving the oxidation behaviour of tungsten [11] and at enhancing its irradiation resistance by nano-structuring [12]. A recent study [13] has been focused on the determination of the optimum Cr concentration range in W-Cr binary thin film alloys for achieving lower oxidation rates though the development of an effective protective layer, leading to values between 10 and 16 wt.%. In addition, thin films of the system W-Cr-Y recently produced by magnetron sputtering were shown to exhibit lower oxidation rate by isothermal oxidation than similar alloys of the W-Cr-Ti system [14]. The high affinity of Y to oxygen can contribute to reduce the oxygen impurity content from the grain boundaries (GB) due to its oxygen getter effect, thus contributing to reduce the ductile-to-brittle transition temperature (DBTT) of tungsten [15]. Furthermore, the addition of up to 1.5 wt.% Y to tungsten inhibits grain growth resulting in grain size refinement [15-17] due to the pinning effect of finely dispersed $Y_2O_3$ nanoparticles in the W matrix. From all previously mentioned, alloys of the W-Cr-Y system appear to be especially attractive for first wall armour application.

In this work, alloys with different compositions of the system W-Cr-Ti as well as new binary and ternary systems, W-Cr and W-Cr-Y respectively, are studied. The alloys are manufactured by MA followed by can encapsulation and HIP. The W–Cr phase diagram is characterized by a miscibility gap below 1677°C (1950 K), leading to decomposition of the high-temperature bcc solid solution into a Cr-rich and a W-rich solid solution phases, known as spinodal decomposition [18]. In the case of the W-Cr-Ti samples, a subsequent thermal treatment at a temperature above the corresponding decomposition temperature is performed after HIP to achieve a single bcc phase microstructure. In this way the presence of the Cr-rich phase, more prone to oxidation than the W-rich phase [4,9], is avoided, and the oxidation resistance of the alloy is expected to be improved; the presence of a single W-rich bcc phase is also preferred in view of an improved mechanical behaviour, since misfit strains and thermal stresses induced by the second phase are avoided. Microstructural investigations, thermal conductivity and microhardness of the alloys after HIP and after the subsequent thermal treatment (only for the W-Cr-Ti system) are presented. A summary of the results of different tests is shown: oxidation tests at various conditions, high heat flux (HHF) tests at GLADIS (Garching Large Divertor Sample Test Facility) [19] as a first "proof of principle" test according to the expected load at the blanket first wall, and thermo-shock tests at JUDITH-1 (Juelich Divertor Test Facility Hot Cells) [20] to simulate conditions under mitigated disruptions in a DEMO-like device.

## 2. Experimental details

Elemental powders of pure W (99.95%, 15-30 μm), Cr (99.95%, 74 μm), Ti (99.5%, 40 μm) and Y (99.9%, 20-30 μm) were used to produce samples of composition W-10Cr-2Ti, W-15Cr and W-12Cr-0.5Y in wt.% (corresponding to W-27Cr-6Ti, W-38Cr and W-32Cr-0.8Y in at.%). The starting powders were mechanically alloyed under Ar in a planetary ball mill Retsch PM400 using WC grinding jars and balls. The MA parameters were those found as optimum for W-Cr-Ti systems in previous works [4-5]. Metallic capsules of Ø 15 mm and 40 mm height filled with the alloyed powder were evacuated, degassed at high vacuum, sealed and HIPed at 1220 °C (1493 K) for 2 h at 150 MPa. The oxygen and nitrogen contents after MA and HIPing were determined using the inert gas fusion method (ASTM E1569, measured with a LECO TC-400), and the carbon content by the combustion method (ASTM E1019, measured with a LECO CS-200). Powders and bulk samples were characterized by field emission gun SEM (FEG-SEM), energy dispersive X-ray spectroscopy (EDS) and X-ray diffraction (XRD). The relative density of the samples was determined from the geometrical and theoretical densities. The average grain size of the dense materials was determined by quantitative metallography. Vickers microhardness of the HIPed materials was measured applying a load of 0.5 kg for 5 seconds. The thermal conductivity up to 900 °C (1173 K) was obtained by the laser flash method. A thermal treatment (TT) on W-10Cr-2Ti HIPed samples was performed at 1600 °C (1873 K) in $H_2$.

Isothermal oxidation tests at 800°C (1073 K) for up to 60 h were performed by thermogravimetric analysis (TGA). Besides, tests under accident-like conditions were also performed. These tests consist of a preheating in Ar up to 600°C (873 K) followed by oxidation in a mixture of 80 vol.% argon and 20 vol.% oxygen ($H_2O$ content $\leq$ 3 ppm) at linear increasing temperature from 600 to 1000°C (873 to 1273 K) during about 17 h, two isothermal oxidation steps in air at 1000°C (1273 K) for 1 h, each of them followed by isothermal steps in Ar at 1000°C (1273 K) for 1 h, and cooling down in Ar. Preliminary HHF tests at GLADIS were performed on an as-HIPed W-10Cr-2Ti sample of dimensions $10 \times 5 \times 6$ mm$^3$ by applying 30 pulses of 2 MW/m$^2$ for 2 s with a neutral hydrogen beam, according to the power load expected at the first wall [2]. The 2 s pulse duration was chosen to achieve 1000°C (1273 K) surface temperature at the end of the pulse. The samples were not actively cooled and thus, a cooling time of 7 minutes after each pulse was required to prevent overheating. The adiabatic loading generates high temperature gradients, which allow a preliminary assessment of the thermo-mechanical behaviour of the material. Besides, the relatively long cooling time permits to evaluate the thermal stability of the bulk structure and possible grain growth.

Thermo-shock tests were performed at the electron beam facility JUDITH-1 [20] on an as-HIPed W-10Cr-2Ti sample and on a W-10Cr-2Ti sample after HIP and TT at 1600°C (1873 K). The samples, of dimensions $10 \times 10 \times 4$ mm$^3$, were exposed to 100 pulses of a power density of 0.38 GW/m$^2$ for 1 ms at a base temperature of 400°C (673 K). These conditions correspond to a heat flux factor (HF) of 12 MW/m$^2$ · s$^{1/2}$ (heat flux factor $= P_{ab}\sqrt{t}\cdot$) which is a measure of the temperature increase:

$$\Delta T = 2 \cdot P_{ab} \sqrt{\frac{t}{\pi \cdot \lambda \cdot c_p \cdot \rho}}$$

Therein, $P_{ab}$ is the absorbed power density, $t$ the pulse duration and $\lambda$, $\rho$ and $c$ are thermal conductivity, density and specific heat, respectively. The base temperature is achieved by means of a heated graphite holder, which is electronically controlled via a thermocouple. To ensure an almost homogeneous loading, a small area ($4 \times 4$ mm$^2$) was scanned with a focused electron beam (beam diameter ~1 mm) at very high scanning frequencies ($f_x = 40$ kHz, $f_y = 31$ kHz). After exposure, the samples were investigated by optical microscopy and SEM. Additionally, the cross section of the samples was analyzed by metallography to study the crack propagation into the bulk material.

## 3. Results and discussion

Mechanically alloyed powders of composition W-15Cr, W-10Cr-2Ti and W-12Cr-0.5Y in wt.% were can encapsulated and HIPed at 1220 °C (1493 K) for 2 h achieving relative densities above 99%, i.e. the material obtained can be considered fully dense within the experimental error. In Table 1 the relative density as well as the O, C and N contents of the as-HIPped materials are shown, which are comparable to those reported in previous works [5,6].

### 3.1. Microstructure

The microstructure of the three alloys is compared in Fig. 1. A very fine and homogeneous microstructure can be appreciated in all systems, with two main phases identified by EDS as a W-rich phase with Cr in solution (bright grey majority phase) and a

Please cite this article as: A. Calvo et al., Manufacturing and testing of self-passivating tungsten alloys of different composition, Nuclear Materials and Energy (2016), http://dx.doi.org/10.1016/j.nme.2016.06.002