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Self-passivating tungsten alloys of the system W-Cr-Y for high temperature applications

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ABSTRACT

Self-passivating tungsten based alloys for the first wall armor 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. This work analyses the oxidation and thermal shock resistance of W-Cr-Y alloys obtained by mechanical alloying followed by HIPing. Alloys with different Cr and Y contents are produced in fully dense form with nanocrystalline or ultrafine-grained microstructure and a dispersion of Y-rich oxide nanoparticles located mainly at the grain boundaries. Isothermal oxidation experiments confirm an excellent oxidation resistance due to the formation of protective oxide scales at the very surface. These layers mainly consist of Cr_2O_3 and mixed Y-W and Cr-W oxides. The superior oxidation resistance of these alloys is confirmed by tests simulating accident-like conditions. The thermal conductivity of these alloys at 600–1000 °C is 2–3 times higher than standard Ni-base superalloys like Inconel-718. The material also exhibits outstanding thermal shock resistance: 1000 pulses of 0.19 GW/m^2 power density and 1 ms duration at 400 °C base temperature resulted in no damage, while an increased power density of 0.38 GW/m^2 resulted in the formation of a crack-network and slight surface roughening. An additional thermal treatment at 1550 °C improves slightly the oxidation resistance and significantly the thermal shock resistance of the alloy.

1. Introduction

The highest melting point among all metals and a comparably high thermal conductivity make tungsten (W) very attractive for many high temperature applications such as power generation, concentrated solar power, target of spallation sources, and plasma-facing materials (PFM) of future fusion reactors among others. However, the poor oxidation resistance of W limits its use either to a vacuum environment or to temperatures below 500 °C in oxidizing environments. In the application as PFM for future fusion reactors such as DEMO (a demonstration power plant considered the previous step for a commercial reactor), W will be exposed to high steady state heat loads in the MW/m^2 range, especially at the so-called divertor [1], but the high oxidation rate of W does not represent a concern in a deuterium-tritium plasma environment under normal operation conditions. However, a loss-of-coolant accident (LOCA) with simultaneous air ingress into the vacuum vessel would lead to a temperature rise of the in-vessel components between 1000 and 1200 °C (depending on the reactor design) within a view to tens of days due to the nuclear afterheat [2]. Under this situation, the use of pure W in DEMO represents a safety risk since part of the W would oxidize forming volatile WO_3 with the potential release of significant amounts of highly radioactively activated species. A possible solution to this important safety issue is the addition of oxide forming alloying elements to pure W, resulting in the growth of a stable protective oxide scale that prevents W from oxidation at high temperatures in presence of oxygen. Under normal operation, the surface of these self-passivating alloys will consist of pure W due to preferential sputtering of the alloying elements by hydrogen isotopes coming from the fusion plasma. A proper selection of the alloying elements is crucial for fusion application since they have to exhibit sufficiently low activation

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by neutron irradiation from the plasma, in addition to other important properties such as low volume increase of the oxides, low vapor pressure, high melting point and no formation of undesirable intermetalics. For this reason, alloying elements forming stable oxides like Al, Nb or Ni are not permitted because of their high activation by neutrons.

During the last years significant efforts were undertaken to develop self-passivating W alloys for fusion application, starting from thin films of the systems W-Cr-Si and W-Cr-Ti [3,4] which served as "model materials" for the manufacturing of bulk alloys by powder metallurgical (PM) routes [5,6]. More recently, it has been demonstrated that W alloys of the system W-Cr-Y result in a significant reduction of the oxidation rate at temperatures up to 1000 °C compared to previously studied ternary systems [7,8]. Besides, the addition of Y leads to the formation of a Y_2O_3 nanodispersion which inhibits grain growth and acts as reinforcement, as reported also in [9,10] for pure W.

In this work the most recent developments on self-passivating alloys of the system W-Cr-Y manufactured by PM for application at the DEMO blanket first wall are presented. The purpose of this research is to develop a W-based material with good oxidation resistance due to self-passivation up to at least 1000 °C, together with as high as possible thermal conductivity and high mechanical strength. In this way, the material should be able to withstand not only the expected thermal load during normal plasma operation, but also transient thermal loads like the so-called edge localized modes (ELMs), during which a large amount of energy is loaded on the PFMs in a very short time [11]. Results on W-Cr-Y alloys with different Cr and Y contents, manufactured by mechanical alloying (MA) and densified by Hot Isostatic Pressing (HIP), are presented. The alloys are subjected to a subsequent heat treatment at 1550 °C, i.e. above the spinodal decomposition temperature of the W-Cr phase diagram, to dissolve the Cr-rich phase and achieve a single bcc phase [12]. By this means, thermal stresses induced by the second phase, which may appear during thermal shock loads, are avoided [7,13]. Microstructural investigations and microhardness of the as-HIPed and HIP + HTed materials are shown and compared to alloys of previous investigations. Thermal conductivity and flexural strength, results of oxidation tests under isothermal and accident-like conditions, as well as thermal shock tests at JUDITH-1 (Juelich Divertor Test Facility Hot Cells) [14] simulating loads under transient events are included.

2. Experimental

Elemental powders of pure W (99.95%, 15–30 μm), Cr (99.95%, 74 μm) and Y (99.9%, 20–30 μm) were used to produce samples of the W-Cr-Y system with Cr contents of 8 and 10 wt.% and Y contents of 0.3, 0.5 and 1 wt.%. The starting powders were mechanically alloyed under Ar atmosphere in a planetary ball mill using WC grinding jars and balls. The MA parameters were optimized to obtain a homogeneously alloyed powder at the minimum milling time to keep impurities from jars and balls as low as possible. Metallic capsules with the alloyed powder were evacuated, degassed, sealed and HIPed at 1250 °C for 2 h at 150 MPa. After HIP a heat treatment (HT) was performed at 1550 °C under H_2 atmosphere. The oxygen and nitrogen contents of powders and bulk materials were determined using the inert gas fusion method (ASTM E1569), and the carbon content by the combustion method (ASTM E1019). Powders and bulk samples were characterized by field emission scanning electron microscopy (FE-SEM) and energy dispersive X-ray spectroscopy (EDS). 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. The Vickers microhardness was measured applying a load of 0.5 kg for 5 s. Three-point bending tests (3PBT) were performed on smooth and single edge laser-notched beams [15] of nominal dimensions $1.8 \times 1.8 \times 20\,mm^3$ over the temperature range 20–1100 °C under high vacuum. All tests were performed in displacement control at a fixed loading rate of 100 μm/min with a 16 mm span width. Flexural strength was computed by Euler–Bernoulli equations for slender beams up to failure. However, when yield stress was exceeded, the 0.2% strength offset was reported. Fracture toughness, i.e. the stress intensity factor for mode I stress, was then computed from the critical load and the beam section using the equation proposed by Guinea et al. [16]. The thermal conductivity was measured by the laser flash method.

Isothermal oxidation tests at 800 °C and 1000 °C for up to 60 h were performed by thermogravimetric analysis (TGA) using a mixture of 80% Ar and 20% O_2 at atmospheric pressure. The mass gain of the samples due to oxide formation was measured by a thermobalance with a sensitivity of 0.025 μg. The procedure is described in detail in [4]. Besides, oxidation tests simulating accident-like conditions were also performed. These tests consist of a preheating in Ar 6.0 up to 600 °C followed by oxidation in a mixture of 80 vol.% Ar and 20 vol.% O_2 at linear increasing temperature from 600 to 1000 °C during about 17 h, two isothermal oxidation steps in air at 1000 °C for 1 h, each of them followed by isothermal steps in Ar 6.0 at 1000 °C for 1 h, and cooling down in Ar. Surfaces and cross sections of the oxidized samples were analyzed by FE-SEM, EDS and Focused Ion Beam (FIB).

Thermal shock tests were performed at the electron beam facility JUDITH-1 [14] on samples of dimensions $10 \times 10 \times 4\,mm^3$, which were exposed at a base temperature of 400 °C to loads consisting of 1000 pulses with power densities of 0.19 and 0.38 GW/m^2 for 1 ms simulating the conditions expected at the divertor under ELMs. To ensure a homogeneous loading, a small area ($4 \times 4\,mm^2$) was scanned with a focused electron beam at very high scanning frequencies. After exposure, the surface and cross section of the samples were investigated by optical microscopy.

3. Results and discussion

Mechanically alloyed powders of compositions (in wt.%) W-8Cr-0.5Y, W-10Cr-0.3Y, W-10Cr-0.5Y and W-10Cr-1Y (corresponding to W-23Cr-0.9Y, W-28Cr-0.5Y, W-28Cr-0.8Y and W-28Cr-1.6Y in at.%, respectively) were can encapsulated and HIPed at 1250 °C for 2 h, achieving relative densities > 99% (Table 1), i.e. the materials are fully dense within the experimental error. The contents of interstitial elements after MA amount to 1200–1500 ppm for oxygen, 100–160 ppm for nitrogen and 200–400 ppm for carbon, and remain the same after HIP.

Besides, a HT after HIP was performed on alloy W-10Cr-0.5Y at 1550 °C, i.e. at a temperature above the spinodal decomposition of the W-Cr phase diagram, see Fig. 1. According to this phase diagram, after HIPing at 1250 °C two bcc phases are formed: a (αW,Cr) main phase with minor presence of (αCr,W). The compositions of these two phases were estimated from the shift of the peaks obtained by X-ray diffraction (XRD) with respect to the pure W and Cr peaks. These compositions are indicated by the blue lines in the phase diagram of Fig. 1, and agree well with the predictions of the phase diagram at 1250 °C. The purpose of this HT is to dissolve the Cr-rich phase, more prone to oxidation, and to produce a single phase material (see red cross and lines in Fig. 1) in

Table 1
Relative density, average grain size and microhardness of W-Cr-Y alloys of different compositions after HIP at 1250 °C and after subsequent HT at 1550 °C (only for W-10Cr-0.5Y).

Alloy composition	HT at 1550 °C	Relative density (%)	Average grain size (μm)	Microhardness	
				Alloys ($HV_{0.5}$)	Pure W (HV) [21]
W-8Cr-0.5Y	No	99.1	102 ± 3	1265 ± 4	1340
W-10Cr-0.3Y	No	99.8	84 ± 3	1145 ± 3	1441
W-10Cr-0.5Y	No	99.8	110 ± 4	1220 ± 8	1304
W-10Cr-1Y	No	99.6	228 ± 8	1190 ± 8	1012
W-10Cr-0.5Y	Yes	98.7	230 ± 11	980 ± 6	1009