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Short Communication

Synthesis and hydrogen plasma interaction of model mixed materials for fusion

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ARTICLE INFO

Article history:
Received 14 April 2014
Received in revised form
3 August 2014
Accepted 10 August 2014
Available online 8 September 2014

Keywords:
Hydrogen plasma
Tungsten
Materials properties
Mixed materials
Carbon/magnesium impurities

ABSTRACT

Samples of mixed materials relevant to fusion (W/C/Mg, where Mg is a chemical stand-in for Be) have been synthesized by planetary ball milling. We explore here W-rich compounds, and investigate their structural and physico-chemical properties, both before and after hydrogen plasma exposure. After presenting the synthesis method experimental results are detailed: clear differences between incorporation of magnesium and/or carbon into a tungsten matrix are observed, as reflected in the specific surface area of the samples and their lattice parameters. Indeed, specific surface area decreases with increasing Mg content but increases with C content. The same trend is seen for the lattice parameter. A particular effect seen after hydrogen plasma exposure is attributed to the presence of magnesium which may also occur in the presence of beryllium.

Introduction

Understanding the interaction of materials with hydrogen is a key issue towards the safe use and generalization of hydrogen as an energy carrier. For instance, in dedicated storage systems [1,2], adsorption and the mechanical resistance of the tank materials (e.g. metal hydrides such as magnesium-based compounds [3–5]) must be optimized. Pipeline materials, such as mixed steels [6–8], to be used for hydrogen transportation, should have a high resistance to aging and mechanical changes.

Both of these phenomena, aging and storage, are also found in the context of the exposure of armor materials in fusion devices to hydrogen plasmas. The long term behavior of these materials in this demanding environment represents one of the main issues to be resolved for fusion power to be realized. The main candidate materials currently considered are beryllium and tungsten, and related alloys [9].

Indeed, it is foreseeable that, under the important energy and particle fluxes that they'll bear, these materials will erode. The erosion products thus generated will then be ejected into the plasma and transported by it to other parts of the vessel [10], where they may re-deposit onto the wall, thus forming layers of mixed and variable (in time and space) compositions

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http://dx.doi.org/10.1016/j.ijhydene.2014.08.021

[11,12]. These layers will be formed under high-energy conditions, far from chemical equilibrium, and with a large range in chemical compositions.

It is therefore important that a database be established that provides the fusion community with a set of relevant properties for such mixed materials layers. These properties are needed both from a theoretical and operational point of view. For instance, they are needed in order to build comprehensive models of plasma-wall interactions to predict the rate of impurity material exchange between the wall and the plasma (see e.g. Ref. [13]) as well as that of hydrogen retention in the plasma facing component (PFCs) and their surface layers [14–16]. First contributions for this database have been obtained by growing mixed layers by the PVD method [17,18,26]. This method provide the tool to study the interaction of layers of interest deposits (W/Be/C).

In order however to synthesize such mixed materials far from chemical equilibrium, other methods are needed. In this paper, we use the planetary ball milling method, also known as mechano-synthesis, to produce gram quantities of mixed materials powders in order to study their behavior under hydrogen plasma exposure. The ball milling method is known to allow incorporation of alloying elements, through severe plastic deformation, above their theoretical maximum solubility as predicted by phase diagrams [19]. These represent conditions of high energy input far from chemical equilibrium, but still provide control over the chemical composition. This thus allows us to begin a systematic exploration of these materials and their structural and morphological properties. We begin by studying their intrinsic structural properties, including specific surface area and lattice spacing, before exposing them to an Electron Cyclotron Resonance (ECR) hydrogen plasma [20].

As described in Ref. [21,25], dust production in tokamaks can occur along several pathways. These include delamination, ejections of molten metal droplets, homogeneous growth in the plasma phase, and layer growth on the PFC's surface from plasma impurity bombardment. Our synthesis method by ball milling aims to address only the type of "dusty" material formed by the latter process.

Experimental set-up

We used a Pulverisette P7 (Fritsch) planetary ball mill in which we ground calibrated amounts of W, C, and Mg powders. Commercial W (purity of 99.9%, particle size 12 microns), C graphite (VWR, particle size < 44 μm) and Mg (purity of 99.8%, particle size < 44 μm) were used as the raw powder materials. We chose to replace the Be actually present in fusion devices by the chemically similar Mg for safety reasons. We expect C to also be present as many PFC's designs, use CFC as backbone on which the armor materials are deposited. The grinding balls were made of tungsten carbide (WC), with a mass ratio between balls and powder content in the mixing jar (Ball-to-Powder Ration, BPR) of 40:1. Unless stated otherwise, the powders were first dry-milled for 22 h to incorporate the add-on element(s) and then in ethanol for another 22 h, always at 350 rpm, to reduce the final particle size (as ethanol prevents shock-induced welding of the particles).With this procedure, we synthesized a total of 21 samples, spanning the W-rich corner in chemical composition of the W/C/Mg ternary diagram, in steps of 2at%, up to a total of 10at% C + Mg. These material compositions are representative of expected deposits in the divertor volume, in particular in places where parasitic plasmas are likely to be present (e.g. under the dome).

For the sake of comparison, another method has also been used, involving magnesio-reduction, i.e. a shock-induced chemical reaction using magnesium to reduce tungsten trioxide, following the reaction scheme:

$$WO_3 + 3Mg \rightarrow W + 3MgO.$$

Due to the high exothermicity of the reaction, the time required to complete the reaction is of the order of ten minutes when a proper amount of reaction moderator (here, salt) is introduced; samples are then leached using 2M HCl solution at 50 °C for 2 h while stirred to remove the magnesium oxide, and then filtered using 220 nm filters to extract the particles from the solution. Sample characterization was performed using X-Ray Diffraction (XRD), followed by Rietveld refinement of the patterns, giving access to the lattice parameter, and to crystallite size and microstrain ratio, using the Isotropic Model in the MAUD program ("Materials Analysis Using Diffraction"). At the same time, specific surface areas (SSA) were measured using the BET method by nitrogen adsorption (COULTER SA 3100). Assuming spherical particles, one can determine their average size from the measured SSA ($m^2\ g^{-1}$) using:

$$R_{particle} = \frac{3}{\rho \cdot SSA} \quad (1)$$

where ρ ($g\ m^{-3}$) is the material's mass density and $R_{particle}$(m) is the average particle radius. Eq. (1) only provides a rough approximation of the particle size and does not take into account agglomeration.

Plasma exposure experiments were carried out in a reactor with a single dipolar ECR source, which can deliver a power of 180 W and generate high density hydrogen plasmas at low pressure. We worked at 10^{-2} mbar, and the plasma parameters are measured by a cylindrical Langmuir probe (Smart probe Scientific System). The typical electron density and temperature achieved are ~10^{10} cm^{-3} and ~2 eV, respectively. The samples were placed on a Macor support for electric insulation, putting them at the floating potential, and situated 3 cm away from the ECR resonance location during 6 h of plasma discharge time, the estimated sample temperature being around 500 K. The mixed materials samples, both before and after hydrogen exposition, were imaged by Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM).

Experimental results and discussion

Intrinsic properties of the samples

Tungsten is the dominant material in the various compounds obtained. Therefore, to establish a first baseline, a morphological and structural study was made to determine the influence of grinding time on particle size and surface condition of a pure tungsten sample.