Journal of Nuclear Materials 493 (2017) 442–447

Contents lists available at ScienceDirect

Journal of Nuclear Materials

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

Effects of the implantation of Sn ions on W matrix's chemical state, crystal structure and hardness

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ARTICLE INFO

Article history:
Received 21 March 2017
Received in revised form
19 June 2017
Accepted 29 June 2017
Available online 30 June 2017

Keywords:
Tin
Tungsten
Ion implantation
Point defects
Chemical shift

ABSTRACT

Prior to the practical application of liquid metals as facing material for fusion reactor, the nature of the interaction layer between liquid metal and tungsten substrate should be studied deeply. In the present work, by means of ion implantation technique using a metal vapor vacuum arc source (MEVVA), Sn ions were injected into a W matrix and a W-Sn modified layer was prepared. The chemical state, crystal structure and nano-indentation hardness of the modified layer were investigated and characterized with the use of X-ray photoelectron spectroscopy (XPS), an X-ray diffractometer (XRD) and a nano-indentor. The results indicate that, after the injection of Sn ions into the W matrix, Sn atoms interacted intensively with W, leading to the generation of a large number of point defects (such as vacancies and self-interstitial atoms) and the decrease of average grain size from 16.7 to 11.9 nm. Additionally, chemical shifts appeared, i.e., the binding energy values of W $4f_{7/2}$, W $4f_{5/2}$, W $5p_{3/2}$ and W $4p_{1/2}$ in the modified layer was reduced by 0.3 eV, 0.3 eV, 0.4 eV, 1–1.4 eV, respectively. The binding energy values of Sn $3d_{5/2}$ and Sn $3d_{3/2}$ decreased, with a chemical shift of 0.6–0.7 eV and 0.1–0.3 eV, respectively. The nano-indentation hardness of the modified layer was enhanced; specifically, when the indentation depth was 26.3 nm, the hardness reached a peak value of 13.8 GPa. In the modified layer, the surface chemical states are quite complex, mainly including SnO, WO_3, SnO_2 and WC.

1. Introduction

As a rare and refractory metal, tungsten (W) exhibits a series of advantages mainly including the possession of a high melting point, excellent corrosion resistance performance and thermal stress resistance performance, as well as favorable mechanical properties [1–4]. Owing to these excellent properties, W is now widely applied in many important industrial fields such as hard alloys, surface hardening materials, electronic functional materials and aerospace materials. When a fusion device operates, the facing materials will suffer from constant bombardment and erosion from the high-flux particle flow [1]. As described above, W has many unique properties and can satisfy the requirements of a facing material. Tin (Sn) is a metal characterized by a low melting point, favorable malleability and stable chemical properties, and as such is commonly used for making alloys. Moreover, Sn can also be used in the preparation of fusion facing materials so as to reduce the damages it suffers. W and Sn are difficult to be fused into an alloy since their formation enthalpy is positive during the alloying process. However, under the bombardment of energetic ions - for example, when the fusion device operates Sn can be deposited on the surface of W in the form of energetic ions or atoms. In addition, the surface of the same metal can significantly improve its wettability.

The use of W as a facing material still confronts a series of challenging problems. For example, W is a brittle material and has a low ductile-brittle transition temperature [1]; under fusion conditions, the hardness and strength of W will decline [4]; a few impurities in W may cause plasma flameout [5]; as a facing material, W will sustain a battery of problems such as neutron damage, corrosion, fusion, catalysis, *etc.*; furthermore, the retention of deuterium in W will severely affect its service life, plasma behaviors and the safety of any fusion reaction [5,6]. To address these problems, the researchers have proposed a variety of solutions. Zhang et al. have prepared ultra-fine grained pure tungsten for enhancing W's hardness and flexure strength [7]. The researchers also found

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http://dx.doi.org/10.1016/j.jnucmat.2017.06.037
0022-3115/

that some oxide particles such as La_2O_3 and Y_2O_3 can improve the W matrix's mechanical properties, toughness, and resistance to thermal load [8–10]. Additionally, for the W matrix, resistance performance to radiation can be heightened after the addition of TiC particles [11]. Although there have been a lot of studies regarding W-based solid facing materials to date, the ideal materials which can meet the requirements in a fusion environment have yet to be found. The study and preparation of a novel fusion material (that is a material which can be applied within a fusion environment) is extremely important to the development of a fusion device in future [12]. Previous research has indicated that liquid lithium (Li), liquid Sn, liquid gallium (Ga) and Li-Sn alloy are all ideal candidates for facing materials. Liquid Li is the one with by far the most promise, but liquid Sn exhibits its own peculiar advantages. Firstly, liquid Sn can add to the improvement of thermal efficiency in the energy conversion process on account of its fairly low vapor pressure [13]. Secondly, compared with liquid Li, liquid Sn has a lower evaporation rate and loss ratio [14]. Therefore, a comparatively high temperature is permissible on the surface of Sn even without the consideration of re-deposition. Thirdly, it is still not clear whether liquid Li has fuel residences; however, with regard to liquid Sn, it is not easy to form hydrides. On the other hand, there are few experimental and theoretical studies on the fusion of Sn and W and the formation of composites. After liquid Sn is added to W, the induced changes in its structure and properties as well as the principle of the interaction mechanisms are still beyond our knowledge, but they are quite critical for investigations on the systems composed of these two materials.

By means of ion implantation technique, Sn ions can be injected into a W matrix to form a W-Sn modified layer. As has been demonstrated, ion implantation can bring about different kinds of complex defects such as vacancy, dislocation and interstitial atoms, which make the issue more complicated. In this article, using an MEVVA ion implantation technique, Sn ions were injected into W and a modified layer was formed. The variations in its chemical state, chemical component and crystal structure were studied in detail, and the effects on its surface properties were also investigated.

2. Experimental methods

The W matrix adopted in the present experiment was prepared using the powder metallurgic method, with a purity of 99.5%. The area of W is 1×2 cm^2. After being ground and polished, the W matrix was cleaned with alcohol and then dried. The adopted Sn cylinder was processed by using Sn particles with a purity of 99.999%. The arc discharge was generated in the metal vapor vacuum arc source (MEVVA) by utilizing the pulses between anode and cathode, and then Sn ions were evaporated, ionized and extracted to form an ion beam. After being accelerated by the porous extraction electrode, the ion beam was injected into the surface of W. In the experiments, the pressure of the vacuum chamber is 5×10^{-4} Pa; the ion accelerating voltage is 40.0 kV; the arc-strike current is 80.0 A; the average ion current is 1.0 mA; the impulse frequency is 20.0 Hz; the pulse width is 1.0 ms and the dose of ions is 5×10^{17} ion/cm^2. The working temperature was always maintained around between 100° and 150°. The implanted ions contain Sn^{+2} and Sn^{+4} ions. The Sn implantation into W was simulated by the SRIM2013 program. The injection energy is set to 80 keV, corresponding to the experimental acceleration voltage. The total number of Sn ions was chosen to 10^5. The results show that the concentration distribution of Sn atoms had a Gaussian distributionin the W matrix, and the distribution peak of the concentration appeared at the depth of ~ 10 nm from the surface, and the maximum implantation depth is about 60 nm. The vacancy distribution peak formed by ion implantation was found by simulation to appear at the depth of ~6 nm.

The multifunctional surface analysis system (ESCALAB250, Thermo VG Co. Ltd, United States) was used in these experiments for performing X-ray photoelectron spectroscopy (XPS) analysis. The primary working parameters are described below: an Al-Ka ray with an energy of 1486.6 eV is used; the power is 150 W (specifically, the values of high voltage and current are 15 kV and 10 mA); the diameter of the spot is 500 μm; the electron kinetic energy is 50.0 eV and the step length of the energy is 0.1 eV. The samples were scanned at different times during the sputtering process. The valence-state analysis of X-ray photoelectron spectroscopy was performed using the binding energy of C 1s (284.6 eV) as the benchmark, and the depth distribution was calibrated based on the sputtering rate of 0.1 nm/s. The nano-indenter (MTS Nano Indenter® XP, United States) was adopted in the experiments for measuring the nano-indentation hardness of the W surface and the W-Sn modified layer. For each sample, 9 points were selected for measurement and an average value was taken. Then the changing curve of hardness with a variation in depth was obtained. The X-ray diffractometer (D8 DISCOVER, Bruker Co. Ltd. Germany) was used for analyzing the phase structure of the modified layer. The primary parameters include: the radiation source is the Cu-Kα-ray at 0.15406 nm; the grazing incidence angle is 1°; the voltage and current of the S-type ray tube are 40 kV and 40 mA, respectively; the sweep speed is 0.02°/s; the sweep integral time is 0.5 s/step and the scanned area extends from 20° to 80°. According to Scherrer's formula, the lattice size of the samples before and after the injection of Sn can be calculated and thereby the effects of the injection of Sn ions on the lattice structure of W can be compared and studied. Scherrer's formula can be expressed as:

$$D = K\lambda/(B\cos\theta)$$

in which K denotes Scherrer's constant, with a value of 0.943, D denotes the grain size (nm), B denotes the half-width height, θ denotes the diffraction angle and λ denotes the wavelength of X-ray.

3. Results and discussion

3.1. Analysis of chemical states

In X-ray photoelectron spectroscopy, the X-ray is used to excite the inner electrons of atoms. The total energy of a photon is consumed in three parts: the energy $\mathbf{E_b}$ (namely, electron binding energy), which is used to excite electrons from an inner shell transition to the Fermi level, the second part $\mathbf{W_S}$ (namely, work function) which is used to excite an election from the Fermi level, the third part $\mathbf{E_k}$ ($=\mathbf{h\nu} - E_b - W_s$ where, ν is the frequency, h is Planck constant), the kinetic energy which the free photoelectron carries. The bind energy is related to the electron concentration in the outer layer of atom; the smaller the former is, the higher the latter is, and vice versa. According to this principle, the chemical shift can characterize the chemical state of the elements in the alloy layer [15]. Fig. 1 shows the curves of depth distribution of W, Sn, C and O in the W-Sn modified layer by XPS depth analysis. As can be seen that Sn ions indeed have been injected into the W matrix and the Sn concentration peak appears near surface within 10-nm depth, the Sn concentration on W surface is about 8.5 at.%. With the depth increasing, the Sn concentration gradually decreases to 6 at.%. In depth for 100 nm, Sn is close to zero. Fig. 2 shows the full spectrum of XPS on surface (red) and 12-nm depth (green) of the W-Sn layer. The binding energy peaks of W, Sn, C and O are found, which also indicate the W-Sn layer has a certain amount of O, C