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Thermal evolution of helium in magnetron sputtered titanium films

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ABSTRACT

Helium-containing titanium films synthesized by magnetron sputtering method were investigated using thermal desorption spectrometry (TDS), transmission electron microscopy (TEM), and scanning electron microscopy (SEM). Helium evolution behaviors under thermal treatment from room temperature to 1500 °C were characterized. Four peaks appeared in TDS at around 100, 420, 700, and 1250 °C were identified and attributed to helium desorption from the specimen surface, substitutional helium (helium atom in a vacancy), small He_mV_n clusters with different helium-to-vacancy ratios, and helium bubbles or voids, respectively. The helium evolution under thermal treatment composed of two coexisting and competing processes, where the faster process dominated in relevant temperature range, i.e. helium diffusion and release at low temperatures, and bubble or void formation at high temperatures. Three characteristic temperatures in TDS were identified in description of the phenomenon.

1. Introduction

The nuclei transmutation either through nuclear reactions between energetic particles and nucleus or through decay of tritium released from metal tritides produces helium isotope. In addition to their insolubility and extremely low diffusion activation energy in metals [1,2], the produced helium atoms have a tendency of self-trapping [3], and a strong binding with lattice defects of vacancies, dislocations, and grain boundaries. Therefore, high concentration helium atoms in metals are inclined to diffuse to and aggregate at lattice defects, forming cavities (including bubbles and voids), especially under high temperatures. These helium-filled cavities can substantially deteriorate mechanical properties of the metals, resulting in lattice distortion, swelling and surface blistering, namely, helium embrittlement [4]. Therefore, the behavior of helium in metals is directly related to the safety of the materials used in the nuclear technology, fusion energy research, and experimental work involving tritium, and the study of helium evolution in relevant materials becomes an inevitable issue for the development of nuclear industry.

The helium isotopes are often introduced into metals to simulate the helium build-up in nuclear reactions and tritium decay process for experimental research, such as radioactive decay of tritium [5], neutron irradiation [6], and ion implantation [7]. However, the introduction of helium through ion implantation is a "violent" method, which is comparable to that of nuclear reaction but quite different from that of the "gentle" method of tritium decay. The two methods give different microstructural environments due to vacancies, induced dislocations and defects, etc., and their study gives different information about the behavior of helium in solids. In general, the helium in tritium materials has a distribution following that of tritium and causes little lattice damage, but covers a high range of concentration, and its production rate decreases exponentially. Whereas the helium introduced via implantation or nuclear reaction causes a large number of defects and has a low concentration range [8]. As tritium is rare and its decay requires too long time, and that normally implanted helium causes high concentration of damages which play a crucial role in helium evolution [9], a magnetron sputtering method with low implantation energy for introduction of helium has been developed to simulate the helium evolution process in metals, e.g. gold films containing high helium concentration (>10 at.%) has been achieved [10].

Titanium has been an important metal for storage of hydrogen isotopes and other applications in nuclear industry, hence been studied intensively over the past few decades [11]. However, up to now the detailed characterization of the microstructure evolution of the helium-containing titanium films is still lacking. In particular, the evolution of cavities in the titanium films prepared by magnetron sputtering method has not been adequately addressed. Therefore, in this paper, we present the studies on helium-containing titanium films prepared by magnetron sputtering and annealing treatments. The studies intend to reveal temperature effect on helium behavior in the films, and provide

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new understanding of helium in metals, which could somehow contribute to finding ways in inhibiting helium embrittlement.

2. Experimental

The helium-containing titanium films were deposited on tantalum (100) and silicon (100) substrates by DC magnetron sputtering method. The background vacuum of the system before deposition was better than 1.8×10^{-3} Pa. The sputtering pressure was 0.6 Pa, and sputtering gas was mixture of high purity helium and argon with different He/Ar flux ratios of 5/40, 60/20, and 60/10 sccm (standard cubic centimeter per minute) respectively, controlled by two mass flowmeters. The sputtering power was 120 W. Each specimen was deposited for 1 h and then kept in vacuum for more than 3 h to cool the film down, as the Ti film would be heated to about 200–300 °C by the ion bombardment during deposition. The films prepared on silicon (100) could be peeled off from the substrates for microstructure analysis.

The contents of helium in the as-deposited films were measured by a LECO RH-404 hydrogen analyzer [12]. The helium concentrations (He/Ti atomic ratio) were determined to be 0.036 (low), 0.105 (medium), and 0.189 (high), respectively for the films prepared under the above three He/Ar flux ratios.

Some as-deposited samples were vacuum annealed for 40 min at different temperatures of 400, 500, and up to 1100 °C, respectively. The thermal desorption spectrometry (TDS) of helium was performed for both the as-deposited and the annealed specimens in a stainless apparatus under linear heating (1 °C/s) from room temperature to 1500 °C. The helium desorption was monitored by a ZQA-402 mass spectra analyzer, and the background vacuum is about 10^{-4} Pa.

The surface morphologies of the samples after TDS treatment were examined by scanning electron microscopy (SEM) (S-3400N, Hitachi corporation of Japan). Some of the samples were also examined by transmission electron microscopy (TEM) using a Tecnai F20 microscope with an accelerating voltage of 200 kV.

3. Results and discussion

The typical TDS curves of the as-deposited samples with low, medium and high helium concentrations are shown in Fig. 1. The TDS curves indicate that the helium release occurs in a wide temperature range from room temperature up to around 1450 °C. There are four main peaks centered at around 100, 420, 700, and 1250 °C in the curves, typical first-order desorption peaks which are hereafter denoted as peaks I, II, III, and IV, respectively. The peak position appears to be independent of helium concentration in the film.

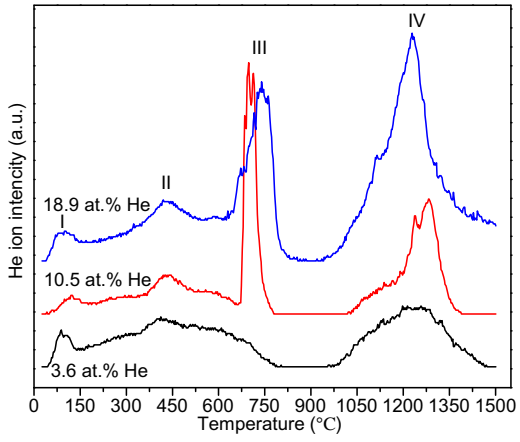

Fig. 1. Thermal desorption spectra of Ti films with low, middle and high helium-concentrations.

Generally, for a TDS curve consisting of several peaks, each peak signifies desorption of helium from a particular type of trapping sites in the sample. To relate a desorption peak to the corresponding type of trapping sites, the mobility of helium at different existential states in the material has to be considered. In the temperature range where the single vacancy is almost immobile, introduced helium is expected to be trapped by the single vacancy. At higher temperatures, however, vacancies and helium atoms become mobile and aggregate into helium bubbles [13]. The main parameters determining the behaviors of helium in materials are the energy of formation, migration, binding, and dissociation of gas atoms in different locations of the crystal lattice. These parameters are difficult to determine experimentally because of the extremely low solubility of helium in metals. Due to the variation in materials and experimental conditions, the number and shape of desorption peaks usually show poor consistency in TDS analyses, whereas the intrinsic helium trapping features may have in common. Kimura et al. [14] measured the TDS of helium-containing ferritic steels consisting of six peaks and suggested that these peaks were attributed to the helium detrapping from the surface, helium-vacancy pairs, dislocations, defects in the γ-phase, α-γ transformation, and helium bubbles, respectively. Vedeneev et al. [15] studied the radiogenic helium thermal desorption from titanium tritide, and observed five peaks of helium release, which were accounted by helium having different states in the lattice: octahedral voids (interstitial solution), vacancies (solution of replacement), small helium clusters, and bubbles within and near the surfaces of titanium tritide grains.

In the present study, peak I would be ascribed to desorption of helium from the specimen surface, as the relevant temperature is as low as around 100 °C [16]. For the peaks II, III and IV at higher temperatures, the activation energies (E) for helium release from the corresponding sites can be calculated based on Redhead's equation of first-order desorption [17]:

$$E = RT_p\left(\ln\frac{T_p\upsilon_1}{\beta} + \ln\frac{1}{\ln\frac{T_p\upsilon_1}{2\beta}}\right), \quad (1)$$

here, R is gas constant, T_p is the peak temperature, υ_1 is the lattice vibrational frequency in the order of the Debye frequency taken as 10^{13} s^{-1}, and β is the heating rate. The calculated activation energies of the peaks II, III and IV are 1.95, 2.77, and 4.41 eV, respectively. A larger activation energy means that it would be harder and require higher temperature for a helium atom to dissociate. It can be assumed that the peak II is corresponding to helium release from vacancies, as its activation energy is in line with the reported dissociation energy of helium atom from a vacancy (1.5 eV) [18]. The α-β phase transformation in titanium takes place around 882 °C while nearly no helium is observed to release at the temperature ranging from 800 °C to 1000 °C, suggesting that the peak III could not be relevant to the phase transformation. Particularly, the peak III should be related to the little He_mV_n (V denotes the vacancy) clusters or pre-existing helium-filled cavities which will be shown in the following TEM analysis. Because of the strong binding energy, the trapping sites responsible for peak IV are believed to be high pressured bubbles or voids formed at the sites like dislocations, grain boundaries or interiors. The calculated activation energy for peak IV (4.41 eV) is coincidently within the range of activation energy of 4.12–4.81 eV for the high temperature release mechanism discussed by Adams and Foiles [19].

The surface morphologies of the samples with different helium concentrations before and after the TDS treatment are shown in