Surface & Coatings Technology 340 (2018) 86–92

Contents lists available at ScienceDirect

Surface & Coatings Technology

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

Fuzzy nanostructure growth on precious metals by He plasma irradiation

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ARTICLE INFO

Keywords:
Plasma irradiation
Nanostructure
Helium bubbles
Precious metals

ABSTRACT

Growth of helium bubbles near the surface of metals leads to various morphology changes when sufficient helium ions are continuously implanted on the surface. In this study, low energy (< 100 eV) helium plasma irradiations to various noble metals were conducted, and consequent surface morphology changes were analyzed. It was found that fiberform nanostructures were formed by the helium plasma irradiation on rhodium and ruthenium thin films, which were deposited by magnetron sputtering, and on platinum and iridium wires. Growth of fiberform structures were not identified on gold, silver, and palladium samples exposed to helium plasmas even though the irradiations were conducted at various surface temperatures, though pinholes were observed on palladium surface. We discussed the relation between the morphology changes and material properties.

1. Introduction

Implanted helium (He) atoms in metals have been known to be trapped, migrate inside the crystal structure, and form clusters and He bubbles [1]. Plasma irradiation experiments under fusion relevant conditions suggested that the implantation can occur even when the incident ion energy is much lower than ~100 eV [2], which is not enough to form defects. Growth of He bubbles led to significant morphology changes on metal surfaces in nanoscale when certain irradiation conditions were satisfied [3–10]. The size and shape of the morphology changes were significantly altered by the material properties and the irradiation conditions, i.e., the melting point, the sputtering yield, the surface temperature, the incident ion energy, the helium flux/fluence and so on. One of the most significant changes found on various metals was the growth of fiberform fuzzy nanostructures [3]. It has been identified that the *fuzz* was grown on W when the surface temperature was in the range of 1000–2000 K and the incident ion energy was higher than ~30 eV [11]; the temperature range was lower for molybdenum (Mo) (800–1050 K) than that on W [12]. In addition, nanocones were formed on titanium (Ti), iron (Fe), and stainless steel [5,13], nano/micro-pillar structures were found on aluminum (Al) and copper(Cu) [6], and cube shaped structures were identified on vanadium (V) [7] after helium plasma irradiation.

On the one hand, the changes in the material properties caused by the morphology change could be harmful for plasma facing component for thermonuclear fusion devices [14]; on the other hand, they could be used for industrial applications utilizing the advantages such as large effective surface area [15] and high optical absorptance [16]. One of the applications of fine structured metals formed by the He plasma irradiation is likely to be photocatalysis/catalysis. Metal oxides and/or (oxi)nitrides are regarded as the material for hydrogen production via solar water splitting [17,18], which can be a solution of the energy problem in the 21st century. It was shown that nanostructured W partially oxidized exhibited significant visible light activity for methylene blue decomposition [5,19] and five times enhanced photocurrent representing water splitting [20].

In this study, we investigated the effects of He plasma irradiation on noble metals. One of the reasons why we focused on noble metals is in the fact that they are regarded as highly active materials as catalysts/photocatalysts. In addition to popular titania supported platinum (Pt) catalysts [21], rhodium (Rh), Pt, and palladium (Pd) have been used to control NO_x [22]. Moreover, gold nanoparticles have been used as various support materials [23], and ruthenium (Ru) and iridium (Ir) are also active catalysts such as for instance electro-catalytic reaction [24]. From He plasma irradiation experiments in a linear plasma device, it is shown that fuzzy nanostructures are grown easily on some metals,

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https://doi.org/10.1016/j.surfcoat.2018.02.026
Received 29 October 2017; Received in revised form 5 February 2018; Accepted 6 February 2018

Table 1
Materials used for experiments: Ru, Rh, Pd, Ag, Ir, Pt, and Au. Atomic number, crystal structure, melting point, boiling point, and shear modulus at room temperature are shown.

	Ruthenium	Rhodium	Palladium	Silver	Iridium	Platinum	Gold
	(Ru)	(Rh)	(Pd)	(Ag)	(Ir)	(Pt)	(Au)
Atomic number	44	45	46	47	77	78	79
Crystal structure	HCP	FCC	FCC	FCC	FCC	FCC	FCC
Melting point [K]	2607	2237	1828	1235	2739	2041	1337
Boiling point [K]	4423	3970	3236	2435	4403	4098	2973
Shear modulus [Gpa]	173	150	44	30	210	61	27

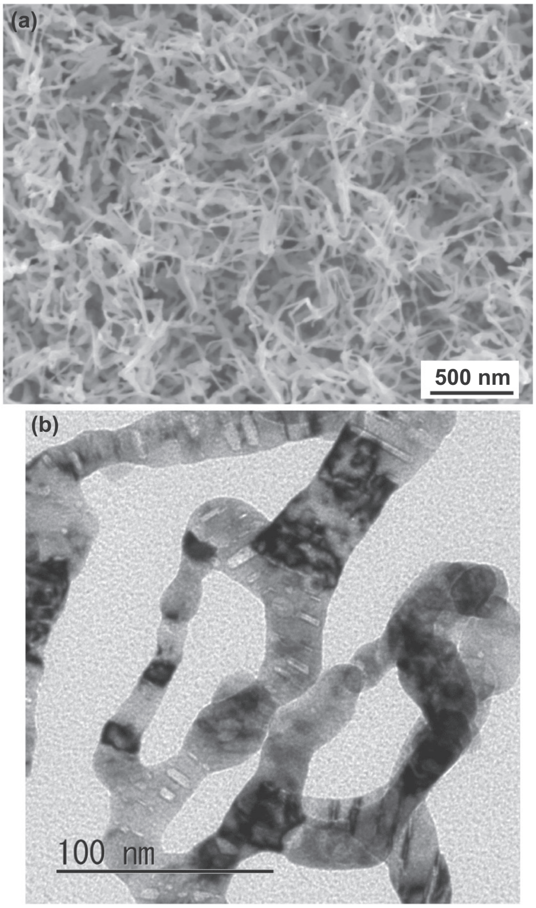

Fig. 1. (a) SEM and (b) TEM micrographs of Rh surface exposed to the He plasma. The irradiation condition was as follows: the incident ion energy of 45 eV, the surface temperature of 973 K, and the He fluence of 1.1×10^{26} m^{-2}.

whereas those fine structures are hardly formed on other metals. Discussion will be provided in terms of the relation between the differences in the morphology changes and physical properties, in particular, shear strength, which is regarded as an important parameter for fuzz growth [25].

2. Preparation

Table 1 summarizes materials used for experiments in the present study: Ru, Rh, Pd, Ag, Ir, Pt, and Au. In addition to the atomic number and crystal structure, the melting point, T_m, the boiling point, and the shear modulus are presented. The atomic number are from 44 to 47 and from 77 to 79. All the materials except for Ru, which has hexagonal close packing crystal (HCP) structure, have face centered cubic (FCC) structure. The melting points of Ru, Rh, Ir, and Pt are higher than 2000 K, while those of Au and Ag are lower than 1500 K. It is worthwhile to note that some metals have significantly high shear modulus; the shear modulus of Ru, Rh and Ir at room temperature is 173, 150, and 210 GPa, which is comparable or higher than that of W (160 GPa).

He plasma irradiation was conducted in the linear plasma device NAGDIS-II (Nagoya Divertor Simulator). The detail of the experimental setup is described elsewhere [5]. The plasma is produced by a direct current (DC) arc discharge using a LaB_6 cathode heated with a carbon heater. Magnetic fields, the strength of which was ~0.1 T, limited the radial plasma diffusion, and linear shaped plasma with the length of ~2.5 m was produced in steady state. The background pressure gas was ~ 10^{-4} Pa or less before the experiments. Additional He gas injection increased the pressure to ~ 0.7 Pa during the He plasma irradiation. The He plasma irradiation was conducted at a downstream region ~1.5 m far from the cathode. Typically the density was on the order of 10^{18} m^{-3}, and the temperature was ~5 eV. The surface temperature, T_s, can be increased to higher than 1000 K without cooling. Thus, the sample was equipped on a water cooling stage with a Mo cover to control the surface temperature when the irradiation was conducted at the temperature of less than 1000 K. The surface temperature was measured by a radiation pyrometer. The incident ion energy, E_i, was controlled by biasing the sample negatively. Note that the space potential of the plasma was about −5 eV, and E_i was determined from the biasing voltage and the space potential. The He flux was measured using an electrostatic probe, which was installed ~ 0.3 m upstream from the sample.

Because some noble metals were expensive and difficult to be obtained as a bulk, we used thin film for Rh and Ru, thickness of which was typically ~1 μm, formed by magnetron sputtering devices. Also, wires were used for Ir, Pt, Au, and Ag similar to Re case in [9]; the diameter of the wires is typically 0.2 mm. Wires were attached to a Mo or Ta plate by a spot wielding; we measured the plate temperature, and the temperature of the wire was assumed to be the same as that of the plate. Plates were used for irradiation experiments on Pd samples, because they were available.

3. Irradiation experiments

3.1. Rhodium, ruthenium, iridium, and platinum

Let us start from metals which have high shear modulus and melting points, i.e., Rh, Ru, and Ir. Fig. 1 (a) shows a scanning electron microscope (SEM) micrograph of Rh surface exposed to the He plasma. The incident ion energy was 45 eV, T_s was 973 K, and the He fluence was 1.1×10^{26} m^{-2}. Fine nanostructures were grown with entangling together on the surface. The shape was slightly different from the fuzzy structures observed on W or Mo; many linearly extended Rh fibers were observed on the surface. For Rh or Ru, He plasma irradiation was conducted using ~1 μm thick samples in this study. The influence of bulk layer was investigated using a W coated Mo samples, and it was shown that mixture of the material occurred around the boundary [26]. In this study, it was confirmed from energy dispersive X-ray spectroscopy (EDS) analysis while conducting cross sectional observation that the surface structures were mainly composed of Rh or Ru under the present condition. No W signal was identified on Rh fiber and W/Ru ratio was less than 10% on Ru fibers. Fig. 1 (b) shows a transmission