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UN_{2-x} layer formed on uranium metal by glow plasma nitriding

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ABSTRACT

Glow plasma nitriding is a simple and economical surface treatment method, and this technology was used to prepare nitride layer on the surface of uranium metal with thickness of several microns. The composition and structure of the nitride layer were analyzed by AES and XRD, indicating that this modified layer is nitrogen-rich uranium nitride, which should be written as UN_{2-x}. TEM images show the nitride layer is composed of nano-sized grains, with compact structure. And XPS analysis indicates there is uranium with abnormal low valence existing in the nitride. After the treated uranium storage in air for a long time, oxygen just entered the surface several nanometers, showing the nitride layer has excellent oxidation resistance. The mechanism of nitride layer formation and low valence uranium appearance is discussed.

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1. Introduction

Uranium metal is mainly used in nuclear and military fields, the main problem which limits its application is this material is easily corroded by oxidation in the air, affecting its performance and polluting environment [1]. Alloying uranium could reduce the corrosion in some extent, but the cost is the decreasement of its nuclear properties and density [2]. At present, surface treatment is mainly used to improve the corrosion resistance of uranium metal. Since uranium is extremely active, its treatment methods usually are PVD or CVD in high vacuum environment [3–5], with expensive equipment and complex process.

In contrast, plasma nitriding is an economical and convenient surface treatment method, and has been applied on conventional materials for years, which can significantly improve corrosion and abrasion resistance of metal surface. A problem restricting the application of this technology to uranium metal is, uranium oxides which always exist on uranium metal surface would prevent the formation of nitrides. And because uranium metal is intolerance to hydrogen corrosion, hydrogen or ammonia could not be used to accelerate the nitriding process. Earlier reports about nitriding treatment on uranium surface, either were carried out under ultra-high vacuum [6], or used some plasma assisted methods [7], that increased costs and complexity of their technology. Here we used a simple and economical glow plasma nitriding method, successfully prepared nitride layer on uranium metal surface with thickness of several microns. Glow plasma nitriding technology is adaptable to the shape of workpieces, and has good prospects for engineering application.

Previous reports about uranium surface nitriding, mostly agreed that nitride formed on uranium surface is α-U_2N_3 or non-stoichiometric α-U_2N_{3+x} [6–9]. However, we found that with thickness of nitride layer increasing, compounds with higher nitrogen content appeared. Comparison of the studies on uranium nitrides by Yeamans [10] and Chinthaka Silva et al. [11], we believe that the nitride phase we found is mainly UN_{2-x}. Previously UN_2 was regarded as intermediate product for the preparation of UN, which has got less attention. We analyzed this nitrogen rich compound, and found some unreported phenomenon.

This paper is structured as follows, Section 2 briefly introduces the glow plasma nitriding technology we used, Section 3 shows analysis of components and structure of the nitride layer, Section 4 discusses the formation mechanism of the nitride layer.

2. Experimental methods

The experiment was carried out in the nitriding furnace that we developed. Schematic diagram of this equipment is shown in Fig. 1. The experimental samples were uranium metal flakes. Before nitriding, the sample surface was mechanically grinded and polished to remove the oxide layer, then cleaned with alcohol. After samples were sent into the vacuum chamber, the base pressure was pumped to 3×10^{-4} Pa. Then high purity nitrogen (purity 99.99%) was fed into the vacuum chamber to the pressure of 50 Pa, and pulse bias of −900 V (frequency 40 kHz, and duty cycle 20%) was applied between the samples and the vacuum chamber wall, forming a glow discharge. Sample temperature was raised to 350 °C by the heating system under the sample stage, and this state was maintained for 4 h.

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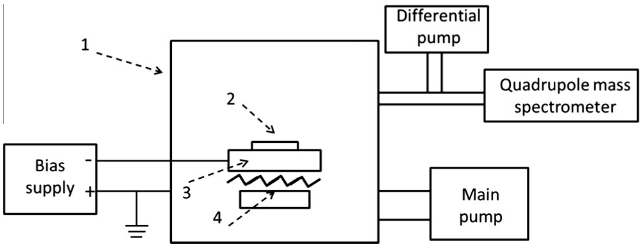

Fig. 1. Schematic diagram of the nitriding furnace. 1. Vacuum chamber; 2. uranium sample; 3. sample stage and 4. heating system.

After nitriding, the samples were analyzed in many ways. The structural properties of the nitride layer were analyzed by XRD in θ–2θ geometry using an X'Pert PRO system with a Cu Kα radiation (λ = 1.5406 Å). The scanning range was from $2\theta = 25°$ to 70°. The experimental data was calibrated by comparing diffraction peaks from single crystal silicon and PDF card. The elements distributions of the nitride layer were investigated by AES depth profiles using a PHI650-SAM system. The cylindrical mirror analyzer (CMA) was adopted for measurements with the electron beam energy of 3 keV and current of 100 nA. During the depth profile process, the sputtering of nitride layers was carried out by a Ar$^+$ ion gun with the energy of 4 keV and the spot size of about 1 mm^2. The chemical states of elements in surfaces were investigated by an ESCALAB 250 system with a base pressure of 5×10^{-8} Pa. Xray photoelectron spectroscopy (XPS) spectra were taken using a mono-chromatized Al Kα radiation (1486.6 eV) and recorded by the hemispherical analyzer with a resolution of 0.05 eV.

3. Results

The sample surface is pale with metallic luster after nitriding. From SEM image (Fig. 2), the surface is compact and smooth, with some particles which might be caused by sputtering. XRD data indicates the surface layer of the sample is uranium nitrides. Two types of structure might exist in the nitrogen-rich uranium nitrides prepared at low temperature. The α-U_2N_3 is bcc Mn_2O_3-type structure, with space group of Ia-3, while UN_2 is fcc CaF_2-type structure with Fm-3m space group. In both structures, uranium atoms pack in the way of face-centered cubic, and nitrogen atoms occupy the tetrahedral sites formed by uranium. The difference is the tetrahedral sites in UN_2 are all occupied by nitrogen, while in α-U_2N_3 3/4 sites are occupied. Although the crystal structure of α-U_2N_3 and UN_2 are very close, the diffraction data from literature shows [12], main diffraction peaks of UN_2 was slightly higher than those of α-U_2N_3. And due to the lattice symmetry of U_2N_3 is somewhat poorer, during the XRD analysis there is more diffraction peaks appeared, as the arrows in Fig. 3 shown. Our XRD data is significantly closer to UN_2 from positions and quantity of diffraction peaks.

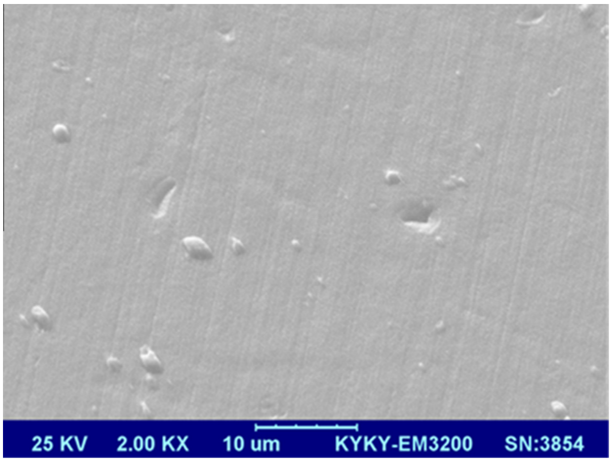

Fig. 2. SEM image of the nitride surface.

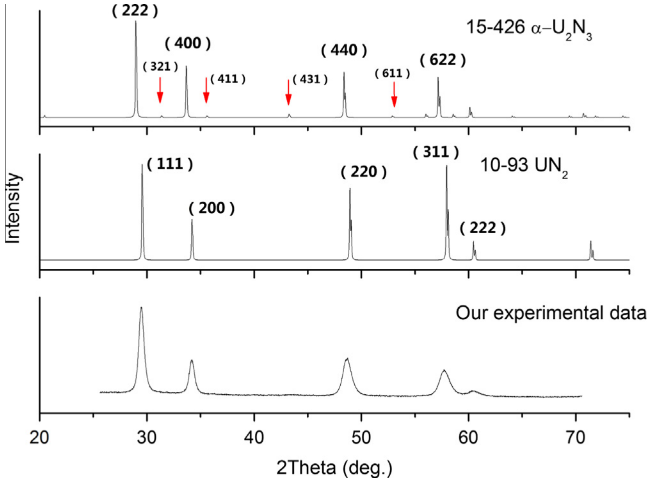

Fig. 3. XRD spectra of α-U_2N_3 and UN_2 from PDF card and experimental data from our nitriding sample.

AES was used to analyze the elements within 60 nm from the sample surface, it could be seen in Fig. 4 that the thin top layer of the sample surface, about 5 nm, is oxidized, which is similar to previously reported uranium nitride surface [6,8]. Below the oxide, nitride composition is stable, where atomic ratio of N/U is about 1.79. From the XRD and AES data, the nitride we prepared is some kind of sub-stoichiometric compound with UN_2 crystal structure, which should be written as UN_{2-x}. From cross-sectional view of the sample (Fig. 5), the thickness of nitride layer is about 5 μm, and the structure is dense. The interface between nitride layer and substrate is clearly seen.

As shown in the above experimental data, a certain thickness of nitride layer was formed on uranium metal surface using glow discharge plasma nitriding method. The modified layer has higher nitrogen content, with compact structure, and is well bonded to the substrate, which can be used as an anti-corrosion layer for uranium metal.

TEM was used to analyze the microstructure of the nitride. It can be seen from Fig. 6(a) and the diffraction rings at the lower right corner, the nitride layer is composed by a number of nano-sized grains. Sample preparation might cause separation of particles, as there are some interfaces in the sample. High resolution

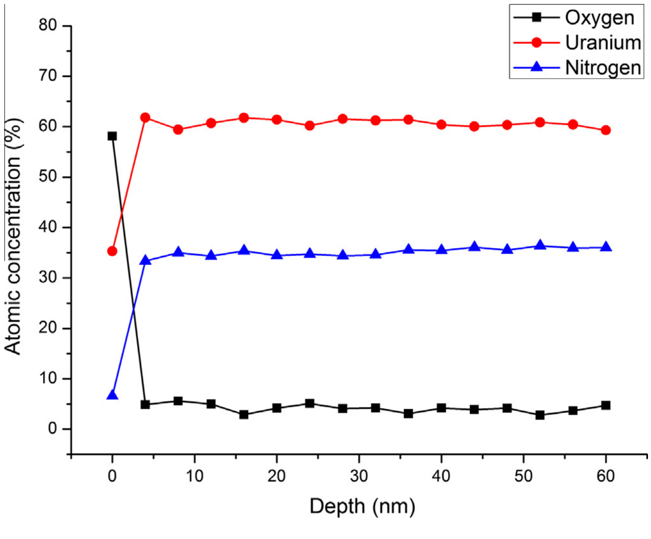

Fig. 4. AES depth profiles of main elements in the nitride layer.

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