Structural analysis of nitride layer formed on uranium metal by glow plasma surface nitriding

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ABSTRACT

The nitride layer was formed on uranium metal by a glow plasma surface nitriding method. The structure and composition of the layer were investigated by X-ray diffraction and Auger electron spectroscopy. The nitride layer mainly consisted of α-phase U_2N_3 nanocrystals with an average grain size about 10–20 nm. Four zones were identified in the layer, which were the oxide surface zone, the nitride mainstay zone, the oxide-existence interface zone, and the nitrogen-diffusion matrix zone. The gradual decrease of binding energies of uranium revealed the transition from oxide to nitride to metal states with the layer depth, while the chemical states of nitrogen and oxygen showed small variation.

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1. Introduction

Uranium has been widely used in the nuclear energy industry due to its attractive properties. The fertile isotope [238]U can capture a neutron converting to fissile [239]Pu with two β decays or directly react with a fast neutron occurred in a fast breeder reactor due to its fissility. Its high Z-number and density ($19.1\,g\,cm^{-3}$ for [238]U) suggest the candidacy in radiation shielding or kinetic energy weapons like penetrators. However, uranium is very active. It is easy to react with most gases in atmosphere. The surface of uranium can be oxidized by the residual oxygen and moisture to form uranium dioxide even in high vacuum [1,2]. Bulk uranium metal will tarnish due to the formation of oxide layer on the surface, and the porous oxide layer will not protect the bulk beneath from the ambient corrosion. The corrosion of uranium greatly affects its physical, chemical, and nuclear properties. Also, the uranium oxide powders can form radioactive aerosol in air, which is a challenge for the environmental security. Thus, the protection of uranium surface is always one of the most important issues in the nuclear engineering field [3,4].

Up to now, several methods have already been used to develop the anti-corrosion systems of uranium, such as organic coatings [5], chemical-plating and electroplating coatings [6,7], and ion plating protective layers [7,8]. Compared with the abovementioned methods, the ion implantation has unique technical advantages, since the surface modification layer will not break off from the matrix due to the formation of gradual transition region between them. The diffusion effect of implanted ions can be enhanced at elevated temperatures, which makes the modified layer thicker for the long-term anti-corrosion. The all-direction ion implantation technology overcomes the sight restriction of the traditional linear ion implantation one, which is very suitable for the complex-shape samples and so has a promising application prospect.

In this work, we present the formation of nitride layer on the uranium surface by the all-direction ion implantation technology. The modified layer is very effective in preventing the matrix from the corrosive erosion. Grazing incidence X-ray diffraction (XRD) and Auger electron spectroscopy (AES) are used to investigate the structural properties of the nitride-modified layer. The chemical states, compositions, and element distribution of the nitride film are studied in detail to understand its formation and behaviors.

2. Experiments

Nitride-modified films were prepared by a glow plasma surface nitriding method on α-phase depleted uranium (>99.7% in content for [238]U) with the diameter of 10 mm and thickness of 3 mm.

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The all-direction ion implantation was adopted in the process. The contents of C and N non-metal impurities in uranium were 200 and 45 ppm, respectively, and the sum of contents of metal impurities was less than 150 ppm. The detailed growth processes of nitride layer are shown as follows. Firstly, the sample was progressively polished with the 1000# abrasive paper as the final one, buffed, ultrasonic cleaned for 3–5 min in ethanol, and dried naturally in the atmosphere. The uranium substrate was quickly put into the vacuum chamber with a base pressure of 5×10^{-7} Pa. Then, Ar was introduced into the chamber with a working pressure of 3–5 Pa. The Ar^+ ions were obtained via the ionization of filament. A pulsed bias voltage of 600–900 V was applied to the sample and the surface was cleaned by Ar^+ ions. After this process, N_2 was introduced into the chamber with a working pressure of 50–60 Pa, producing the plasma by adjusting the arc current of the filament. Finally, a pulsed bias voltage of 500–700 V was applied to the sample for the nitrogen ion implantation. The sample temperature was raised up to 250 °C for 240 min after ion implantation. In such configuration, the nitride layer was about 200–250 nm in thickness. Note that this thickness of the nitride-modified layer is needed to negate the environmental concerns for depleted uranium.

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 ($\lambda = 1.5406$ Å). The scanning range was from $2\theta = 25°$ to $65°$ with a step of $0.05°$, and the scanning time was 1 s for one datum. The Debye–Scherer formula was used to calculate the grain size of the nitride layer. Considering the fact that the signal of the uranium bulk cannot be ruled out from XRD spectra with a conventional incidence angle since the nitride layer is rather thin, we carried out XRD measurements adopting grazing incidence angles of 1 and 3°. The element distributions of the nitride layer and the characteristic Auger peaks of elements 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.

3. Results and discussion

3.1. Phase analysis of nitride layer

The nitride layer on the α-phase depleted uranium (>99.7% in content for ^{238}U) was analyzed by grazing incidence XRD. The obtained spectra are shown in Fig. 1. The penetration depth (L) can be determined by the linear absorption coefficient (μ_l),

$$L = \frac{1}{2\mu_l} \sin \alpha_i \tag{1}$$

here α_i is the grazing incidence angle. The linear absorption coefficients are 6182 cm^{-1} for α-U and 3155 cm^{-1} for UO$_2$. Also, the μ_l is estimated to be 3200 cm^{-1} for U$_2$N$_3$ because its density and structure are similar to UO$_2$. The penetration depths are thus determined to be 27 and 82 nm for $\alpha_i = 1$ and 3°, respectively. In this regard, grazing incidence XRD spectra have the ability to reveal the real structural features of a thin layer on the matrix, and moreover the structural information of the rather thin surface of the layer can be obtained with $\alpha_i = 1°$.

Fig. 1 shows grazing incidence XRD spectra with $\alpha_i = 1$ and 3°. The main phases found in both spectra are α-U$_2$N$_3$ according to the PDF2-2004 standard card. When the grazing incidence angle is 1°, the XRD peaks are mainly from the α-U$_2$N$_3$ phase. There are several weak diffraction peaks in the $\theta = 35$–$40°$ range, which are due to the uranium phase. Also, the UO$_2$ phase can be detected. Thus, the modified layer is composed of the major α-U$_2$N$_3$ phase and the minor uranium and UO$_2$ phases. When the grazing incidence angle
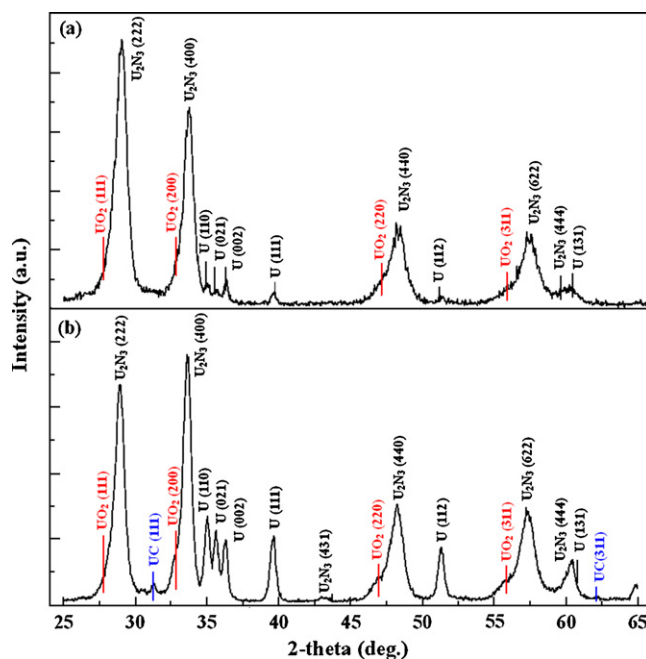

Fig. 1. XRD spectra of the nitride-modified layer on the uranium matrix with grazing incidence angles of 1° (a) and 3° (b).

is 3°, the signal from the α-U$_2$N$_3$ phase still dominates XRD spectra. However, the XRD peaks of uranium are evidently enhanced as compared with those obtained with $\alpha_i = 1°$. The XRD peaks of UO$_2$ also show a slight enhancement, indicating that the detecting depth reaches the interface of the nitride layer and metal matrix. The UO$_2$ phase is enriched at the interface, as identified by AES, which will be discussed below. There are also some weak peaks of UC, which may be the result of the reaction between carbon impurities ($\sim$200 ppm) and uranium in the plasma nitriding process. The XRD results reveal that the nitride layer is rather thin. The content of U$_2$N$_3$ decreases and that of uranium increases as the depth increases in the layer.

The grain size (d) can be derived from XRD using the Debye–Scherer formula,

$$d = \frac{K\lambda}{\beta \cos \theta} \tag{2}$$

where K is the correction factor (0.89), λ is the X-ray wavelength (1.5406 Å), β is the in θ–2θ peak width (corrected for instrumental broadening), and θ is the Bragg diffraction angle. We choose the α-U$_2$N$_3$ (2 2 2) line to calculate the grain size since it is prominent in the involved profiles. The calculated values are about 13 and 16 nm with $\alpha_i = 1°$ and 3°, respectively. In fact, XRD analyses with different grazing incidence angles reveal that the average grain size is always in the range of 10–20 nm. Note that the calculated value may be smaller than the real one. Because the crystal structure and parameters of UO$_2$ are very similar to U$_2$N$_3$, their Bragg diffraction angles are very close. The weak signal of UO$_2$ will exist as the shoulder of the strong U$_2$N$_3$ peak. Also, there is the tensile stress near the surface of the modified layer. Such factors will broaden the XRD peaks, and so make the calculated grain sizes smaller than those in reality [9].

3.2. Composition analysis of nitride layer

Fig. 2 shows the AES depth profiles of the main elements in the nitride layer on the sample surface. Here, the α-phase depleted uranium (>99.7% in content for ^{238}U) was used as the substrate. Four zones are established for different ablation time (t); they are: (I) the