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Fretting wear behavior of nitrogen implanted Zircaloy-4 alloy①

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Abstract: Zircaloy-4 was implanted with nitrogen at 120 keV with various ion doses between 1×10^{13} and 1×10^{14} ions/m^2. Fretting wear tests were performed at various cycles and loads under water immersion condition by the fretting simulator, The implanted surfaces were analyzed by Auger electron spectroscopy (AES) and transmission electron microscope (TEM). Micro-hardness tester measured surface hardness. It is shown that nitrogen implantation produced Zirconium nitride oxide and high density dislocations in implanted layer, surface hardness was enhanced from HK280 for unimplanted specimen to HK1800 for a total ion dose of 1×10^{14} ions/m^2. The nitrogen ion implantation treatment provided significant improvements in the resistance of fretting damage.

Key words: Zircaloy-4; fretting wear; surface hardness; nitrogen implantation **Document code:** A

1 INTRODUCTION

Zircaloy-4 is commonly used for fuel cladding of pressured water reactors (PWR), because it has a low thermal neutron cross section, excellent corrosion resistance, adequate strength and good formability. In a nuclear reactor heat generated in the fuel element is extracted by pumping a fluid coolant continuously through the reactor core. Fretting wear and fatigue between fuel cladding tube and space grid are two of the major failure damages of the tube during operation of nuclear reactor[1,2]. Fretting damage, often a forerunner of fatigue cracking, occurs when tight fitting surfaces are subjected to cyclic relative motion. Even extremely small amplitudes can produce micro-surface damage, which can accumulate and lead to fatigue crack initiation. In general, fretting and abrasion are reduced by increased surface hardness[3]. Lowering the friction coefficient can further improve fretting resistance. Ion implantation is an effective means of hardening component surfaces through the creation of compressive stress in the subsurface regions and formation of hard phase precipitates[4,5]. Preliminary tests and reference have shown that ion implantation holds potential for reducing fretting wear[6,7].

2 EXPERIMENTAL PROCEDURE

The composition of Zircaloy-4 used in the study was as follows: Sn1.24; Fe0.21; Cr0.11; O0.13; Si0.008; Zr98.30(%). The specimens were tubes with outer diameter 10 mm and thickness of wall 1 mm, implanted with the nitrogen ion at 120 keV with different doses ($1\times10^{13}\sim1\times10^{14}$ ions/m^2). Auger energy spectrometer (AES) and transmission electron microscope (TEM) were used to analyze the composition and structure of the specimens, the surface hardness was measured by the MHT-1 micro-hardness tester.

The fretting wear experiment was carried out on the fretting wear tester made by the authors[7]. Two tube specimens were crossed cross contacted and moved each other with a vertical vibration of 10 HZ between ±15 μm with a reciprocating translational movement of 1 mm under water immersion at 20 ℃, The applied load and translational movement cycle ranges for fretting wear were 1 ~ 10 N and 9 000 ~ 360 000 cycles respectively.

3 EXPERIMENTAL RESULTS

3.1 Microstructure and hardness

The original unimplanted specimen of Zircaloy-4 had a homogeneous crystalline structure. The TEM observation has shown that the microstructure was α-phase + homogeneously distributed particles of Zr$[Fe.Cr]_2$[6]. The dislocation density in the unimplanted specimen was lower than that of the nitrogen implanted specimens (Fig.1). Furthermore. The fine precipitates of ZrO_2 and ZrN were observed in the implanting layer (Fig.2). AES has shown that the quantity and implanting depth of N and O were increased with the accumulating of the nitrogen-implanted doses (Fig.3). On the other hand, the experiment has shown that the micro-hardness increased with increasing implanted doses (Fig.4).

3.2 Fretting wear property

Fretting wear between Zircaloy-4 tubes under water immersion is significant under accelerated fret-

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Fig.1 Micrograph of second-phase particles and dislocation in unimplanted Zircaloy-4 alloy

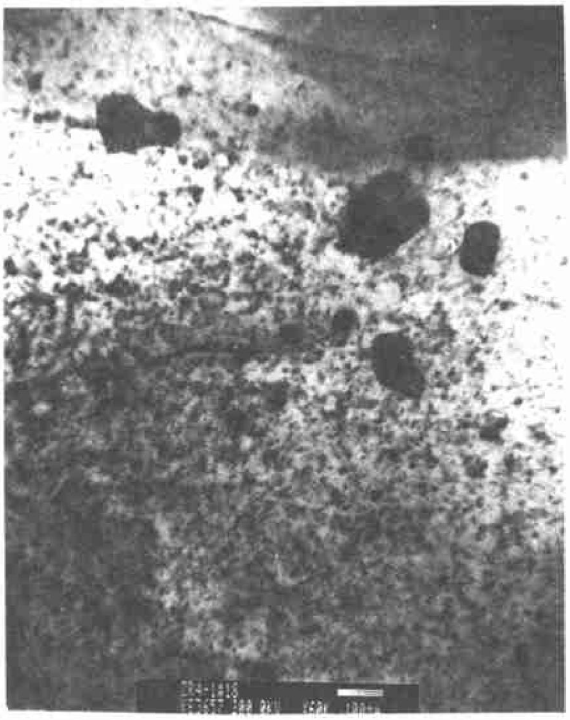

Fig.2 Micrograph of fine particles in an implanted layer

ting wear condition. The abrasive depth of the implanted specimen was obviously lower than that of the unimplanted specimen. Nitrogen implantation at various total ion doses improves gradually fretting wear resistance with increasing implanted doses. An optional improvement is found for the specimen implanted to a total doses of 8×10^{-3} ions/ m^2 Under the same experimental conditions. The depth of the fretting specimen increased with the accumulation of the fretting wear cycles (Fig.5). However, the depth and the width of the fretting crater scars of the implanted specimens were evidently lower and shorter than that of unimplanted specimen. The area of the fretting wear of the former was smaller than that of

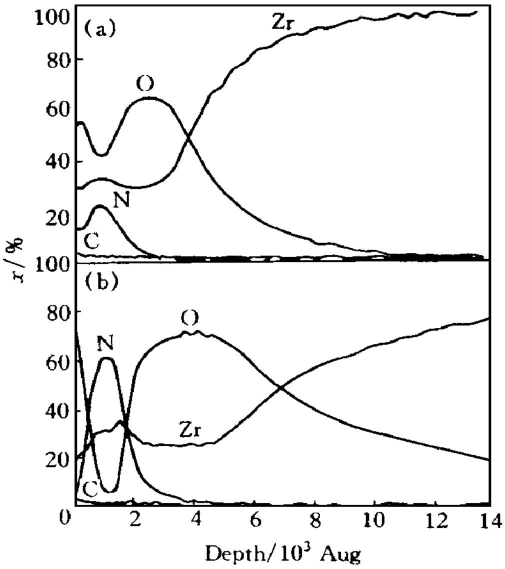

Fig.3 AES depth profiles of nitrogen implanted Zircaloy-4 alloy (sputtering rate 15 nm/min)
(a) —3×10^{13}ions/ m^2 ; (b) —1×10^{14}ions/ m^2

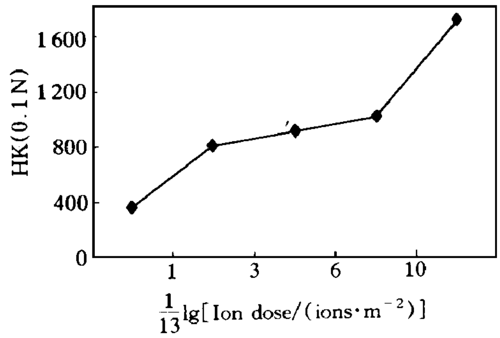

Fig.4 Knoop microhardness(0.1 N) for unimplanted and N^+ implanted Zircaloy-4 alloy at various doses

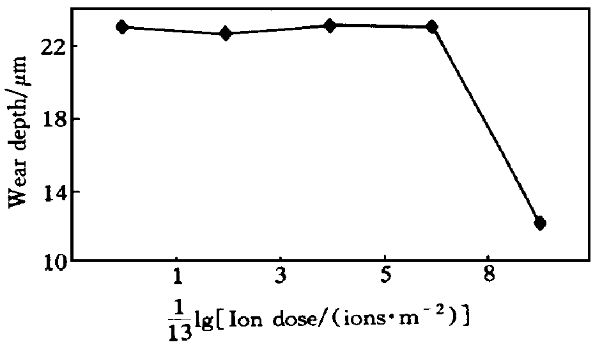

Fig.5 Variation of crater depth for unimplanted and N^+ implanted Zircaloy-4 alloy for various ion doses after fretting wear tests

the later (Fig.6) . The regulations of the two kinds of specimens were similar with increasing the cycle times. Additionally, the debris of the fretting was slivers with obvious parallel furrow-like scars no matter whether the specimen was implanted or not.

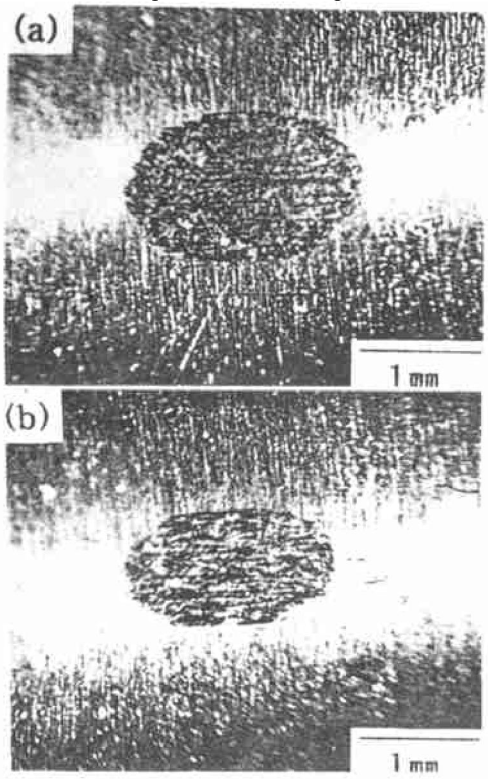

Fig.6 Micrographs of crater scar for unimplanted and N^+ implanted Zircaloy-4 alloy
(a) —Unimplanted;
(b) —N^+ implanted(Doses 3×10^{14} ions/ m^2)

4 ANALYSES AND DISCUSSION

The unimplanted tube specimen of the Zircaloy-4 alloy had a fully recrystallized structure. Many spherical, polygonal, or rectangular and square precipitates of Zr[Cr, Fe]$_2$, through the TEM, are observed in the range of 10 ~ 200 nm, and most of the particles are less than 100 nm in size. Additionally, the dislocation density in the substrate is lower, the elements Fe and Cr in the specimen were mainly distributed in the particles of the intermetallic particles[8]. A series of physical and chemical reactions during nitrogen implantation were triggered in the surface layer. As a consequence, a lot of fine particles of ZrO_2 and ZrN were formed at the surface as the results of above mentioned chemical reactions. With the increase of the implanted doses, the amount of the fine particles would increase simultaneously. The physical changes include the elimination of grain boundaries, the increase of the dislocation density and creation of compressive stress. The chemical and physical changes combine to produce a harder and lower friction[9] surface, which has increased resistance to fretting wear[10].

In the experiment, the surface hardness increases with the increase of nitrogen-implanted doses. The possible reason is due to the formation of hard phase precipitates, such as fine particles of ZrN and ZrO_2 and the introduction of numerous vacancy atoms and distortion of the lattice; the hardness of those fine particles was higher than that of the matrix of the Zircaloy-4 alloy. And consequently, the precipitated strengthening and the boundary strengthening were triggered. Hence, the movement of the dislocation would be impeded, which lead to the result that the hardness of the implanted specimen was increased by 300 % ~ 800 % times comparing with that of the specimen without being implanted. When implanted doses increased, the number of second phase particles increased and the effects of strengthening and hardening were clearly improved. Which will evidently improve the fretting wear resistance of the materials.

Given the morphology of the fretting wear, which is shown to be as multi-parallel furrow-like scars, and its the sizes, depth and volume, it can be seen that the nitrogen implantation has manifestly improved the wear resistance of the materials. According to the mechanism of the fretting wear[12~14], the major factors in producing fretting wear is the additional alternating shear stress in the contact areas arising from the frictional stress occasioned by the oscillatory movement between the contact surface. At the beginning of the cycle, the surface was not smooth, and there was a particular stress concentration, e.g. at the boundary between slip and non-slip region or at (near) the outer contact boundary. Work hardened by the vertical stress and tangential friction force would form and over strain occur at the contact region. Thus, plasticity was lost and some additional abrasive action could occur. As a consequence, many contact spots at the surface of the specimens would be wear off and drop into the depressed regions between the contact spots during the process of fretting. The migration of the debris is the characteristic of the original step of the fretting wear (Fig.7(a)) . With the increase of the wearing scars, the depressed regions were filled up, some spots of metallic contact were worn off, and numerous fine spots comprised a smooth surface (Fig.7(b)) . With the further increase of the debris, the debris accumulated at the surface migrated to the lower place beside the plane (Fig.7(c)) . When several small planes formed a layer of oxide debris, the debris at the center of the contact plane were hard to be removed out due to that the displacement of the relative moving was small, thus lead to a redistribution of the stress at the contacted region. The vertical stress at the center of this region was increased, and the tangential compress at the outer region was decreased due to the escaping of the

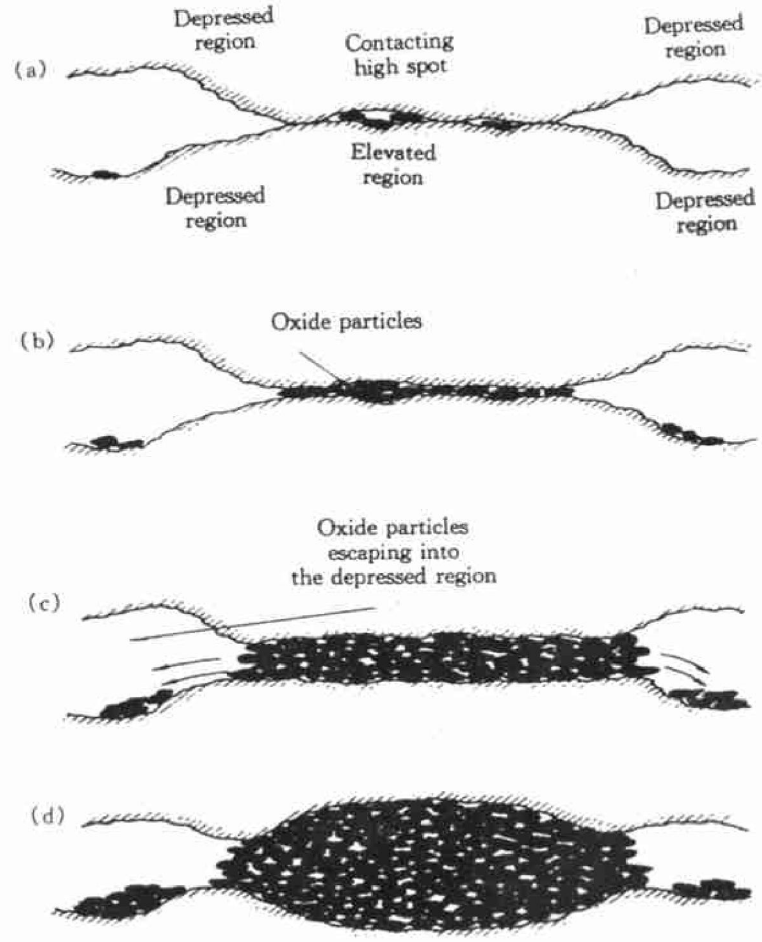

Fig.7 Schematic representation of initiation and spreading of fretting damage
(a) —Accumulation of trapped particles in the space among the high spots;
(b) —Integration of a company of contacting areas into a united area;
(c) —Spilling of particles into the adjoining depressed regions;
(d) —Curved shape of the large pit as the result of stronger abrasive action acting in the central region

debris, i.e. the fretting wear at the center was serious than that of the outer region, the depressed region rapidly deepened, too (Fig.7(d)). Many fine voids conflated into larger ones with the repeat of the processes as above mentioned. When the fretting wear reached a stable stage, the debris produced and moved out at the contact surfaces was equal, and the thickness of the debris between the surfaces was constant, too. Namely, the amount of wearing off during each cycle of fretting was stable, thus, the total amount of wearing off is linearly proportioned to the cycling times.

Plastic deformation (movement of the dislocation) at the fretting wear surface of specimens will occur under the periodical work of the tangential stress and the vertical stress. On such kind of condition, the tangential stress is just the friction force at the surface. According to the calculation of the tangential stress in this experiment, the greatest value of shear stress was located at the subsurface, and decreases with the increase of the depth. Dislocations under the subsurface moved repeatedly under the action of shear force, which lead to the plastic deformation and the cutting and piling up of the dislocations. When the dislocations met some obstacles, such as impurities, second phase particles, boundaries of the phases and some other crystal defects, voids would be produced. Under the continuous action of fretting wear, these voids became the nucleus of the initial crack. When the shear stress is[12]:

$$\tau = 2[\gamma E/D]^{1/2}/\beta$$

where τ is the criteria shear stress, γ is surface energy during the expanding of the cracks, E is the elastic modulus, D is the average diameter, β is a constant depend on the stress. The cracks will spread gradually and some fine cracks will conflat and produce relatively longer cracks. When these cracks reach the surface, slivers of metal bolted from the matrix will be produced. The sliver debris and the multi-layer parallel furrows at a certain depth of the specimen investigated in this experiment proved that the cracks were produced and spread as the process described as above mentioned.

As the above analyses, the hardness and the strength of the implanted layer rapidly were improved after the implantation. Because of the produce of the numerous fine second phase particles and the increase of the defects in the crystal, the criteria value of the shear stress for the formation of the cracks was greatly increased, and the resistance of plastic deformation increased simultaneously. Which lead to the produce of the cracks. The increase of the surface hardness and strength will lead to the lowering of the friction coefficient, which will make the resistance of fretting wear of the implanted specimens better than that of the unimplanted specimen. In a certain range, the greater the implanted doses, the better the effect of strengthening of the implanted layers. Particularly, when the implanting doses reach 8×10^{13} ions/ m^2, under the load of 0.1 N, the max value of the shear stress produced at the subsurface is less than the strength of that region. Hence, the plastic deformation is hard to occur, and the resistance of friction is the most preferable.

5 CONCLUSIONS

1) Numerous fine particles of ZrO_2 and ZrN will produced in the implanted layer after the nitrogen implanted in Zircaloy-4 alloy, which will trigger a lot of dislocations in the layer and precipitation, dislocation and boundary strengthening. With the increase of implanted doses, the number of the particles and the defects in the crystal will increase simultaneously. Thus, the effect of the strengthening will be fortified. The surface hardness will be improved from HK280 before implanting to HK1 800 after implantation.

2) The criteria shear stress in the subsurface under the contacted point will be evidently improved because of the increase of the strength of the ion implanting layers and creation of compressive stress. Thus the plastic deformation in this region is hard to occur and the resistance to the initiation of cracks is improved. Furthermore, the increase of the surface hardness will diminish the friction coefficient.

3) The surface of the Zircaloy-4 alloy, after fretting wear, is characterized of multi-parallel furrow-like scars. The amount of fretting off debris and the times of cycles are approximately linearly proportional no mater whether implanted or not.

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