Improvement of wear resistance of Zircaloy-4 by nitrogen implantation

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ABSTRACT

Nitrogen implantation process has been applied for improvement of wear resistance of Zircaloy-4 fuel cladding materials. Nitrogen was implanted at 120keV to a total dose range of 1×10^{17}ions/㎠ to 1×10^{18}ions/㎠ at various temperatures between 270℃ and 671℃. The microstructure changes by nitrogen implantation were analyzed by XRD and AES and wear behavior was evaluated by performing ball-on-disc type wear testing at various loads and sliding velocities under unlubricated condition.

Nitrogen implantation produced ZrN_X nitride above 3×10^{17}ions/㎠ as well as heavy dislocations, which resluted in an increase in microhardness of the implanted surface of up to 1400 H_k from 200 H_k of unimplanted substrate. Hardness was also found to be increased with increasing implantation temperature up to 1760 H_k at 620℃. The wear resistance was greatly improved as total ion dose and implantation temperature increased.

The effective enhancement of wear resistance at high dose and temperature is believed to be due to the significant hardening associated with high degree of precipitation of Zr nitrides and generation of prismatic dislocation loops.

1. Introduction

The improvement of wear resistance of fuel cladding material is one of the prime concern to avoid the failure of fuel cladding tube and to extend the operation lifetime in pressurized light water nuclear power reactor. Zircaloy-4 is being widely used for a fuel cladding tube in nuclear power reactors.

Nitrogen implantation has been known to be effective process to enhance the tribological properties of various ferrous alloys and other alloys including Al, Ti.[(1)-(5)]

It was reported that nitrogen implantation promoted the formation of fine nitride precipitates as well as prismatic dislocation loops at moderate temperatures, which in turn induced hardening of implanted surface and corresponding wear and friction resistance.[(6)-(10)] Another contribution to hardening by nitrogen implantation has been proposed to be due to dislocation pinning by nitrogen in the tensile stressed region of dislocation during ion implantation.[(11),(12)]

In this study nitrogen implantation process has been applied for precision hardening of Zircaloy-4 and for improving wear resistance. Implantations were carried out at various total ion doses and processing temperatures. The structure change including nitride formation was investigated by AES and XRD. In addition, hardness change and wear behavior were measured by micro-hardness and ball-on-disc type[13] wear testings. Dynamic friction measurement during wear and microscopic observation of wear track and counterball were used to illuminate the wear mechanism.

2. Experiments.

Zircaloy-4 plate of 1mm thickness was implanted with nitrogen ion at various total ion doses and temperatures at 120keV. The detail implantation conditions are listed in Table 1. The nitrogen implanted surface were them analyzed by AES and XRD to study the composition profile and compound formation behavior at the implanted region. Hardness was measured by knoop microhardness testing and wear testing was performed by using ball-on-disc type wear testing system under unlubricated condition in air. AISI 52100 and Al_2O_3 balls were used as counter balls for wear tests. Dynamic friction force change was monitored during wear tests. Wear losses and damage of specimen as well as ball were analyzed by weight-loss measurement and optical microscopic observation, respectively.

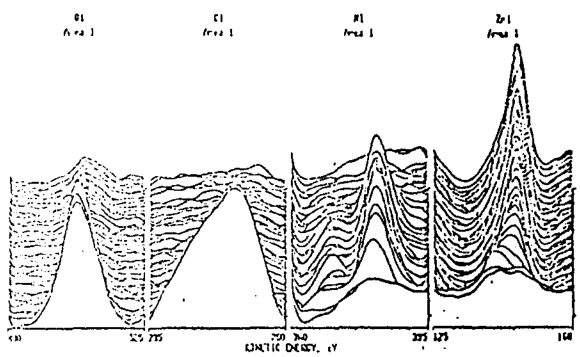
Table. 1. Implantation conditions of plate specimen

Ion dose (ions/㎠) / Implantation condition	1×10^{17}	3×10^{17}				6×10^{17}	1×10^{18}
Processing temp. (℃)	664	270	400	500	620	671	660
Current density (μA/㎠)	92.6	37.04	55.56	69.45	92.6	92.6	92.6

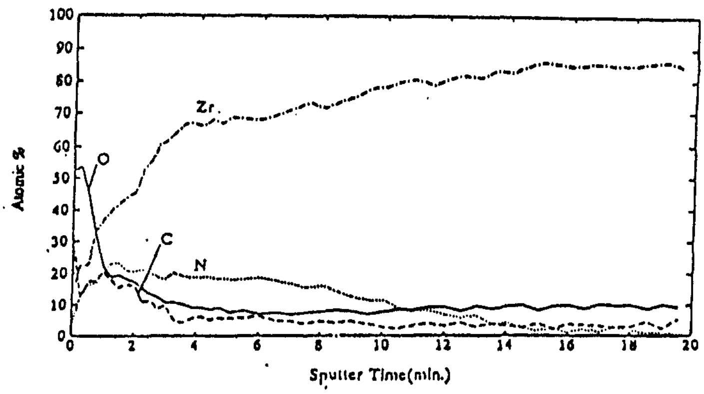
3. Results and Discussion

Fig. 1 illustrated the typical AES depth profile of nitrogen implanted Zircaloy-4 in the study. Nitrogen profile was fairly deviated from typical Gaussian profile as expected from computer simulation. This was believed to be due to the deep penetration associated with radiation enhanced diffusion during nitrogen implantation at elevated temperature of 430℃. The maximum penetration depth of nitrogen was measured to be approximately 7,000Å. In addition, carbon and oxygen contamination was detected in the shallow surface region. Nitrogen implantation at elevated temperature induced the formation of ZrN as shown in Fig. 2. ZrN was found to be formed at 660℃ to a total dose of $3x10^{17}$ions/㎠. The formation temperature of ZrN was reduced to 430℃ by increasing total ion dose to $5x10^{17}$ions/㎠. In other way, ZrN formation was promoted with increasing total ion dose as illustrated in Fig. 3. It was observed that ZrN was produced at the implanted surface to $1x10^{17}$ions/㎠ at 660℃ and XRD peak intensity of ZrN increased with increased total ion dose up to $1x10^{18}$ions/㎠. This suggested that the amount of ZrN formation increased with increasing total ion flux at elevated temperature for nitrogen implanted Zircaloy-4.

Hardness changes with process temperature and total ion dose were shown in Fig. 4 and Fig. 5 respectively. Hardness was largely increased with increasing total ion dose and



(a) Three dimensional depth profiles of auger electron energy



(b) Distribution of element concentration with specimen depth

Fig. 1. AES depth profiles for N^+ ion implanted Zircaloy-4. (120keV, 3×10^{17}ions/㎠, 92.6 μA/㎠, 620℃)

processing temperature. The maximum hardness reached to 1400 to 1600 H_k (10gf) which correspond to hardness improvement by a factor of 4.7 to 5.7. The significant hardness increase by nitrogen implantation at elevated temperature and high ion flux was attributed to promotion of the fine ZrN precipitates as illustrated in XRD analyses (Fig. 2 and Fig. 3). In addition, irradiation hardening associated with defects generation and dislocation pinning by nitrogen and dislocation interaction was believed to provide additional hardening effect to the Zircaloy-4. Fig. 6 and Fig. 7 illustrated the weight loss behaviors through ball-on-disc wear for unimplanted and nitrogen implanted Zircaloy-4 as a function of total ion doses and processing temperatures, respectively.

Nitrogen implantation effectively reduced wear loss against AISI 52100 steel ball and Al_2O_3 ball at all total ion dose range (Fig. 6). It was observed that wear against AISI52100 steel

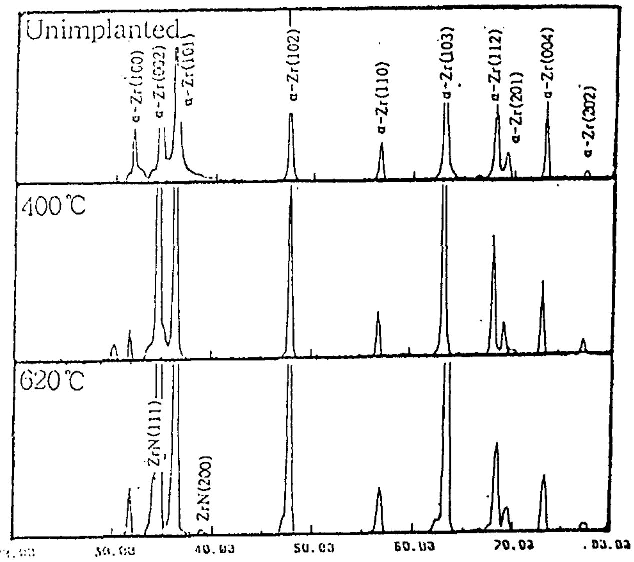


Fig. 2. XRD patterns of Zircaloy-4 substrate and N^+ implanted Zircaloy-4 with various processing temperatures. (120keV, 3×10^{17}ions/㎠)

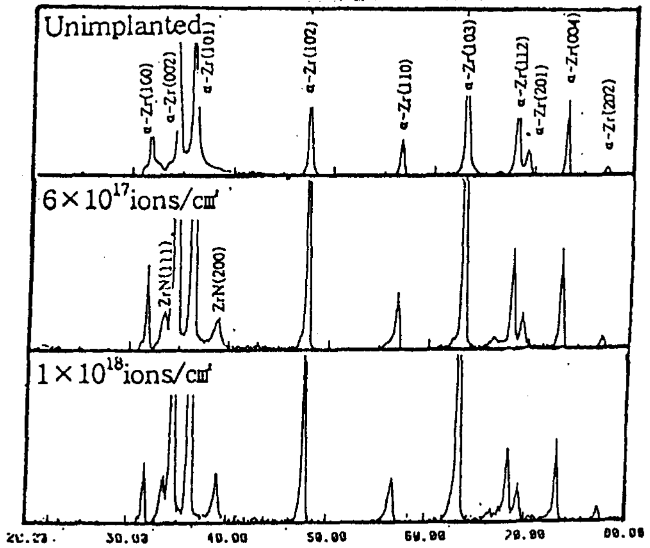


Fig. 3. XRD patterns of Zircaloy-4 substrate and N^+ implanted Zircaloy-4 with various ion doses. (120keV, processing temperature : 660℃)

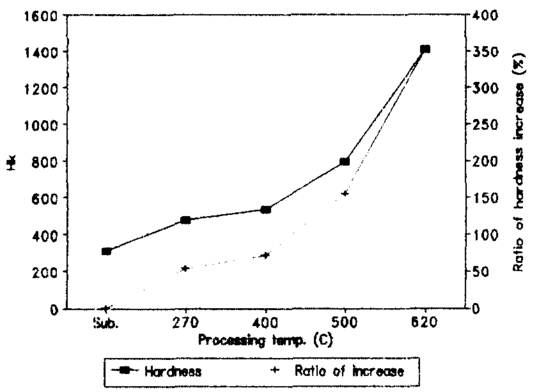


Fig. 4. Micro knoop hardness (10gf) and ratio of increase change for Zircaloy-4 substrate and N^+ implanted Zircaloy-4 with various processing temperatures. (120keV, 3×10^{17}ions/㎠)

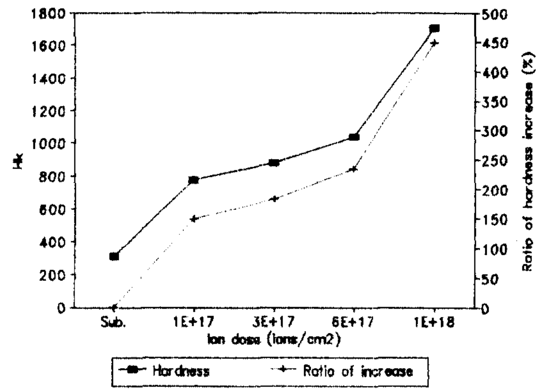


Fig. 5. Micro knoop hardness (10gf) and ratio of increase change for Zircaloy-4 substrate and N^+ implanted Zircaloy-4 with various ion doses. (120keV, processing temperature : 660℃)

ball occurred in a mixture mode of adhesive and abrasive wear which induced weight losses of Zircaloy-4 and AISI 52100 steel ball as shown in Fig. 8. On the cotrary, wear between nitrogen implanted Zircaloy-4 and Al_2O_3 ball decreased increasing total ion doses. Especially Zircaloy-4 implanted to a total dose of 1×10^{18}ions/㎠ showed greatly reduced friction coefficient as shown in Fig. 9 and induced sticking of wear debris onto implanted surface, which in turn resulted in an increase in the total weight of Zircaloy-4 (Fig. 6).

Wear behavior was also affected by implantation temperature. Nitrogen implantation resulted in an reduction in the wear loss against Al_2O_3 ball at all processing temperature while enhancement of wear resistance against AISI 52100 steel ball for Zircaloy-4 implanted above 500℃ (Fig. 7). The detrimental effect on wear resistance against AISI 52100 steel ball for Zircaloy-4 implanted at 270℃ and 400℃ was found to be due to the increase in the friction coefficient as shown in Fig. 10. It was suggested that insufficient hardening by

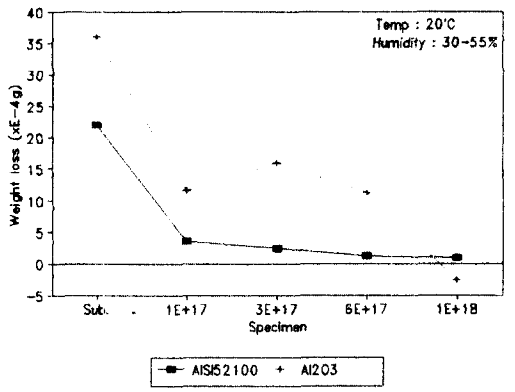


Fig. 6. Variation of weight loss for Zircaloy-4 substrate and N^+ implanted Zircaloy-4 (processing temperature : 660℃) against AISI 52100 ball and Al_2O_3 ball with various ion doses. (50gf, 0.4㎧, 1000m)

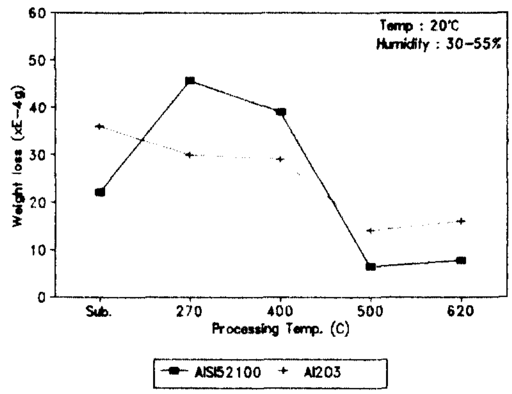


Fig. 7. Variation of weight loss for Zircaloy-4 substrate and N^+ implanted Zircaloy-4 (3×10^{17}ions/㎠) against AISI 52100 ball and Al_2O_3 ball with various ion doses. (50gf, 0.4㎧, 1000m)

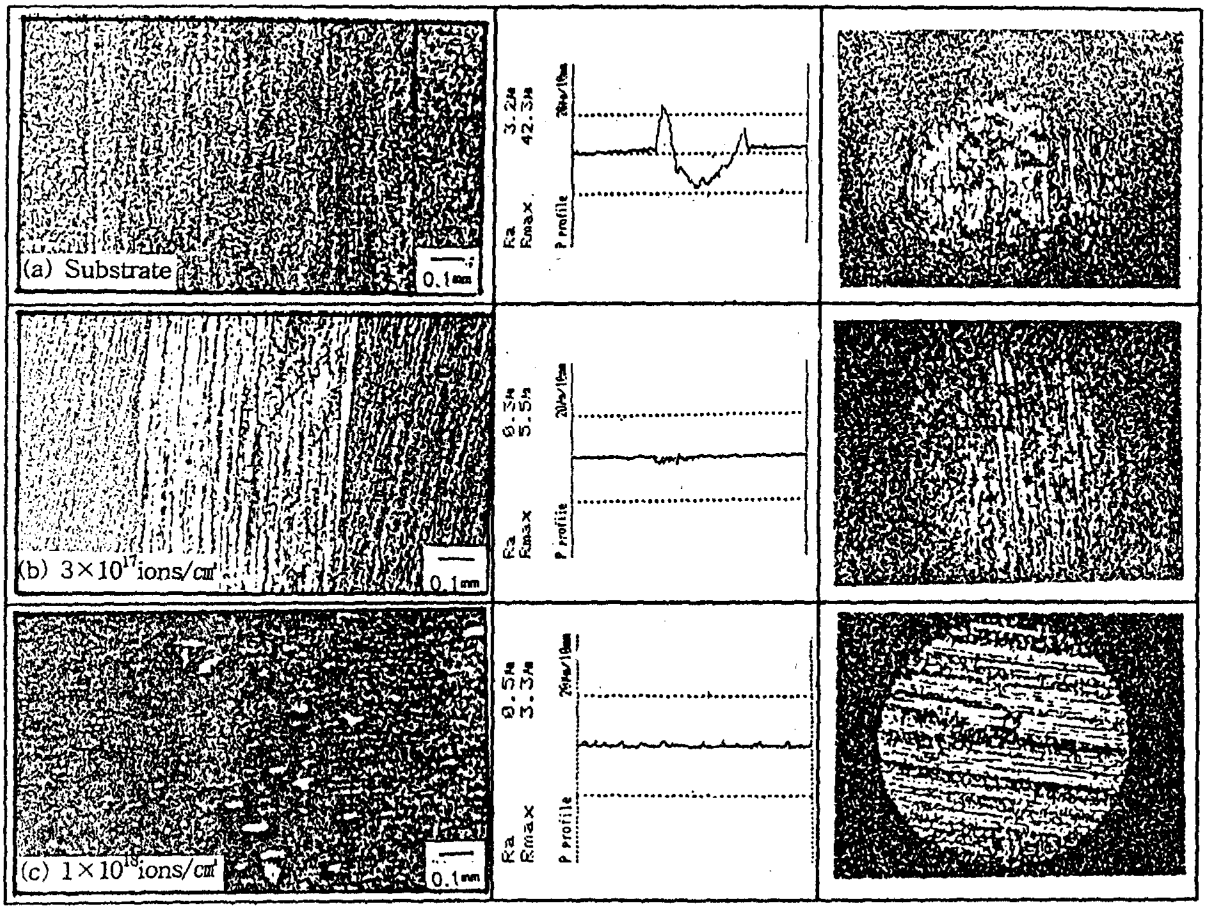


Fig. 8. Optical micrographs of wear scar and counterball and transverse track profile for Zircaloy-4 substrate and N^+ implanted Zircaloy-4 against AISI 52100 ball. (50gf, 0.4m/s, 1000m)

(a) Substrate

(b) 120keV, 3×10^{17}ions/㎠, 620℃

(c) 120keV, 1×10^{18}ions/㎠, 660℃

nitrogen implantation initially promoted the adhesion of AISI 52100 steel ball tip and significantly induced adhesive wear and, thereby increasing wear loss. However, sufficient hardening over 800 H_k compared to hardness 550 H_k of steel ball by nitrogen implantation at 500℃ and 620℃ (Fig. 4) restricted adhesive wear greatly, resulting in enhancement of wear resistance.

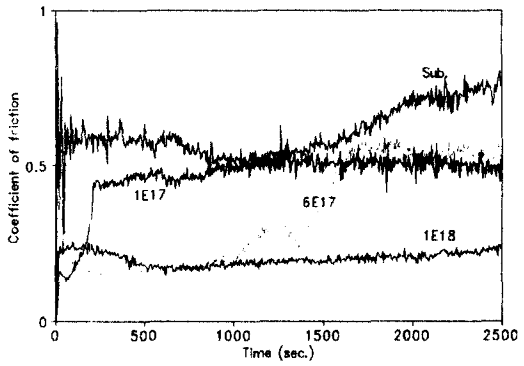


Fig. 9. Variation of dynamic friction coefficient of Zircaloy-4 substrate and N^+ implanted Zircaloy-4 (processing temperature :660℃) against Al_2O_3 ball with various ion doses. (50gf, 0.4㎧, 1000m)

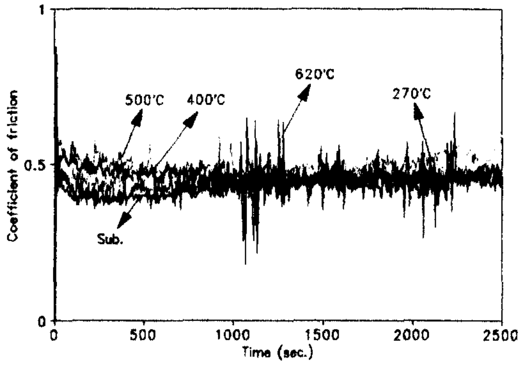


Fig. 10. Variation of dynamic friction coefficient of Zircaloy-4 substrate and N^+ implanted Zircaloy-4 (processing temperature :660℃) against Al_2O_3 ball with various ion doses. (50gf, 0.4㎧, 1000m)

4. Conclusion

Nitrogen implantation onto Zircaloy-4 produced ZrN precipitates above 620℃ and the amount of ZrN precipitates increased with increasing total ion dose at 620℃. The formation of ZrN precipitates greatly enhanced the hardness of Zircaloy-4 by a factor of 5.5 corresponding to 1780 H_k (10gf). The enhancement of hardness reduced wear loss of nitrogen implantation Zircaloy-4. The improvement of wear resistance was significant for Zircaloy-4 implanted to a total dose of 1×10^{18}ions/㎠ at 620℃. These results implied that the significant in wear resistance of Zircalöy-4 by the formation of fine ZrN precipitates in large amount could be obtained by N+ implanted implantation to high total ion dose at high processing temperature.

Reference

1. P. Sioshasi and J. J. Au, Mat. Sci. Eng., 69, 161, 1985
2. R. Hutching, Mat. Sci. Eng., 69, 129, 1985
3. T. Varjoranta, J. Hirvonen and A. Antlila, Thin Solid Films, 75, 241, 1981
4. S. Fayeulle and D. Treheux, Nucl. Inst. Meth., B19/20, 216, 1987
5. H. Dimigen, K. Kobs, R. Leutenecker, H. Russel and P. Eichinger, Mat. Sci. Eng., 69, 181, 1985
6. A. N. Didenko, Yu. P. Sharkeev and A. E. Ligachev, Mat. Sci. Eng., A115, 337, 1989
7. I. L. Singer, Appl. Surf. Sci., 18, 28, 1984
8. O. Popoola, M. F. Denanot, M. Cahoreau, J. P. Villain, P. Moine and J. Caisso, Acta Metall., 37, 867, 1989
9. J. Bently, L. D. Stephenson, R. B. Benson. Jr., P. A. Parrish and J. K. Hivonen, Mat. Res. Soc. Symp. Proc., 27, 151, 1984
10. David M. Fllstaedt, "Ion Implantation and Ion-Beam Mixing", Sandia National Laboratories, Division 1112, Albuquerque, NM, U.S.A.
11. L. J. Bredell and J. B. Malherbe, Thin Solid Films, 125, L25, 1985
12. J. B. Pethica, R. Hutchings and W. C. Oliver, Nucl. Inst. Meth., 209, 995, 1983
13. F. J. Koerber, H. Petersein and H. Ranke, Thin Solid Films, 181, 505, 1989