Accelerated Corrosion of Zircaloy-4 Cladding at High Burnup

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Abstract

Post irradiation examination of the intact and defective fuel rods irradiated for 2 cycles showed that the defective rod had concentrated hydrides on the outer cladding surface at the three-fourth elevations where accelerated corrosion was accompanied. To simulate the effect of tensile stress by fuel swelling, the mini-fuel rods containing a copper rod and alumina pellets were subjected to corrosion testing in a highly lithiated solution at 350 °C. The stressed Zircaloy-4 cladding by the expansion of the copper rod had hydrides concentrated on the outer surface and accelerated corrosion while the unstressed cladding did not. Thus, it is concluded that the fuel swelling imposes tensile stress on Zircaloy-4 cladding to concentrate hydrides on the outer surface, accelerating out- and in-reactor corrosion. Based on this finding, accelerated corrosion of Zircaloy-4 cladding at high burnup in pressurized water reactors is discussed.

1. Introduction

As corrosion of Zircaloy-4 cladding determines the lifetime of light water reactor fuel rods, much attention has been paid to an understanding of the corrosion mechanism and developing the corrosion resistant cladding materials. Among other things, accelerated corrosion at high burnup is a major concern to the integrity of fuel rods at high burnup although its cause is not clearly understood.

Fuel rods irradiated to high burnup has hydrides concentrated locally near the outer surface of Zircaloy-4 cladding [1-3]. This concentration of hydrides is observed only on the upper part of the cladding where the gap between cladding and pellet would be closed. Therefore, it seems that accelerated corrosion at high burnup may be related to the concentrated hydrides near the outer surface adjacent to the oxide front that is, in turn, caused by tensile stress applied by fuel swelling after the closure of the gap.

The purpose of this study is to investigate the effect of tensile stress imposed by fuel swelling on the distribution of hydrides and their effect on corrosion of Zircaloy-4 cladding. The mini-fuel rods containing a copper rod and alumina pellets respectively, were used to investigate the effect of applied tensile stress by fuel swelling. In addition, a defective rod and an intact rod next to it that had the identical operating power histories were selected to demonstrate accelerated in-reactor corrosion of

Zircaloy-4 cladding by hydrides.

2. Experimental procedures

A defective fuel rod and an intact rod next to it were subjected to destructive tests at the post irradiation examination facility of Korea Atomic Energy Research Institute. The selected intact rod turned out to have the same operating power histories as the defective rod. The intact rod had burnup of 17,900 MWd/MTU while the defective rod had burnup of 16,100 MWd/MTU after 2 cycle irradiation. The defective fuel rod was found to have a through-hole of around 2 mm in diameter at a distance of 675 mm from its bottom end. The oxide layer thickness and hydride distribution were metallographically determined at the transverse sections of a fuel rod. The metallographic specimens were prepared by impregnation with resin, cutting, mounting, grinding and then polishing. The quantity of hydrogen in a given cladding tube was measured through a vacuum extraction method by using the LECO RH 404 analyzer.

To simulate the effect of tensile stress on the redistribution of hydrides, two types of min-fuel rods of 55 mm long were made with Zircaloy-4 cladding tubes. One fuel rod contained a copper rod inside to apply tensile stress on the cladding tube during corrosion testing. Because of the larger thermal expansion coefficient of Cu, the cladding tube of the stressed rod was subjected to hoop stress of 66 MPa at 350 °C. The other mini-rods had Al_2O_3 pellets contained inside. Since thermal expansion coefficient of Al_2O_3 pellets is comparable to that of Zircaloy-4 and the Al_2O_3 pellets with the smaller diameter were used, the gap between cladding tube and pellet was not closed at the testing temperature. Consequently, this cladding tube was not subjected to hoop stresses at all during corrosion testing, which is termed the unstressed tube. By welding both the ends of the mini-fuel rods to the end plugs, the fuel rods were sealed so that only the outer surface of the mini-fuel rod was corroded during corrosion testing. Corrosion testing was conducted according to ASTM G2 in a LiOH solution containing 2200 ppm Li at 350 °C or in steam at 400 °C. After corrosion testing, the mini-fuel rods were cooled slowly with the rate of about 18 °C/h enough to eliminate any temperature gradient.

3. Results and discussion

3.1 The concentration of hydrides on the outer surface of the cladding by tensile stress

Fig. 1 shows the distribution of hydrides with the axial elevation for a defective rod. The defective rod had the so-called secondary hydriding at the upper part of the cladding, due to water ingress through a hole near the bottom of the rod. The most severe hydriding occurred at a distance of 2227 and 2518 mm from the hole, corresponding to the three-fourth elevations. The content of hydrogen at this elevation was measured at 1295 to 1502 ppm hydrogen (H). At this upper part where the secondary hydriding occurred, it is to note that hydrides locally become concentrated near the outer surface as shown in Fig. 1b. At a higher elevation, as shown in Fig. 1a, a much less content of hydrides, 345 ppm, was observed.

On the other hand, near the through-hole (Fig. 1c), a few hydrides precipitated uniformly across the section. In contrast, an intact rod next to the defective one had a few hydrides distributed uniformly as shown in Fig. 2, even at the corresponding elevation where the concentration of hydrides occurred in the case of the defective rod. Performance analyses of this rod shows a temperature gradient of 15-39 $^{\circ}$C varying with time and the axial elevation across the cladding thickness under normal operating conditions [4]. However, the fairly uniform distribution of hydrides on the intact rod, as shown in Fig. 2, suggests that the extent of the temperature gradient across the thickness is not enough to cause the concentration of hydrides.

After a through-hole is formed, gap heat transfer and fuel thermal conductivity will be reduced due to the presence of steam in the gap and fuel oxidation, respectively [5, 6]. Since the maximum of the fuel and cladding temperatures is expected to occur at the three-fourth axial elevations, the gap at this elevation will be closed first compared to that at other parts. Thus, the cladding parts only at this elevation are likely subjected to tensile stress by fuel swelling by thermal expansion. Furthermore, the largest amount of hydrogen will be picked up at the hottest part of the cladding because the breakdown process of the oxide layer formed on the inside surface of the cladding depends on temperature and hydrogen partial pressure [7]. This may explain why the secondary hydriding would occur at the hottest part of the cladding. In addition, the tensile stress caused by the fuel swelling is the largest at the three-fourth elevations, facilitating diffusion of hydrogen toward this part. Since the applied tensile stress on the cladding subjects the outer surface to tensile stress and the inner surface to compressive stress [8], the hydrogen will diffuse toward the outer surface from the inner surface [9, 10]. This results in the concentration of the hydrogen on the outer cladding surface. Despite a similar temperature gradient across the cladding thickness along the axial elevation, the concentration of hydrides only at the three-fourth elevations demonstrates that the governing factor to the concentration of hydrides is not a temperature gradient but the tensile stress imposed on the cladding. To the contrast, the fuel temperature of the intact rod is much lower than that of the defective rod. Therefore, the intact rod must have been subjected to no tensile stress at all leading to just a uniform distribution of hydrides.

To simulate the effect of tensile stress by fuel swelling on the distribution of hydrides, two types of min-fuel rods inserted with a copper rod and the Al_2O_3 pellets were corroded in a LiOH solution with 2200 ppm at 350 $^{\circ}$C. Fig. 3 shows the hydride distribution of the stressed and unstressed tubes after corrosion in the highly lithiated solution for 4 days. As expected, the stressed tube had concentrated hydrides preferentially near the outer surface of the cladding. Besides, some hydrides on the outer surface were reoriented in the radial direction as shown in Fig. 3c. In contrast, the unstressed tube had all hydrides distributed uniformly and circumferentially on the cross-section. Since both fuel rods were subjected to corrosion testing under an isothermal condition followed by slow furnace cooling, any temperature gradient effect can be ruled out. This argument is also valid during cooling because no non-uniform distribution of hydrides was observed on the unstressed tube. Based on the simulated results,

thus, it is concluded that the secondary hydriding and local concentration of hydrides on the outer cladding surface on the defective fuel rod, as shown in Fig. 1, are caused by tensile stress by swelling.

The molar volume of zirconium hydride is larger by around 17% than the molar volume of zirconium [11]. Thus, there will be a difference in the chemical potential of hydrogen in a stressed hydride as opposed to that of hydrogen in an unstressed hydride. Even if each hydride is in local equilibrium with the zirconium matrix, there will be thus a driving force for diffusion of hydrogen in the matrix so that hydrogen will move from the compressed or unstressed hydride to the hydride subjected to tensile stress. When the cladding tube is subjected to tensile stress by fuel swelling, the inner cladding surface is under compressive stress and the outer surface is under tensile stress [8]. In other words, the stress gradient between the inner- and outer surfaces of the cladding will have hydrogen diffuse from the inner surface to the outer surface, not only concentrating hydrides on the outer surface but also reorienting hydrides in the radial direction normal to the tensile stress [12-14]. Therefore, a conclusion is drawn that the circumferential tensile stress applied by the expansion of the copper rod (or fuel) causes the concentration of hydrides on the outer cladding surface subjected to tensile stress. There is further evidence that applied stress redistributes hydrogen, resulting in local accumulation of hydrogen close to pellet interfaces on irradiated fuel rods [15]. Therefore, the most probable site for the secondary hydriding of the defective rod is likely the cladding part under the highest tensile stress by fuel swelling such as the location at the three-fourth elevations.

3.2. Accelerated corrosion of Zircaloy-4 cladding by hydrides

Fig. 4 shows the change of the weight gains with time for the unstressed and stressed Zircaloy-4 cladding tubes during corrosion in the highly lithiated solution at 350 °C. The stressed tube had accelerated corrosion leading to higher weight gains as opposed to the unstressed one. The oxide layer thickness after corrosion in the highly lithiated solution for 4 d reached 50 and 41 μm for the stressed tube and the unstressed one, respectively. Fig. 5 shows the enlarged microstructures of the oxide front in the stressed and unstressed tubes. It was found that the oxide front near the radial hydrides advanced farther into the Zircaloy-4 matrix along themselves. Therefore, it is concluded that the highly concentrated hydrides enhance corrosion of Zircaloy-4 cladding. However, the cause for accelerated corrosion by concentrated hydrides is yet to be investigated further. We may just speculate that the enhanced corrosion by hydrides may be related either to faster oxidation of hydrides compared to that of zirconium (Asher and Trowse, 1970) or to the tensile stress state of the outer cladding region covered with many concentrated hydrides.

The above out-reactor results prove that the tensile stress imposed by fuel swelling causes hydrides to locally become concentrated on the outer cladding surface adjacent to the oxide front, accelerated corrosion of Zircaloy-4 cladding. To observe this phenomenon also in reactor conditions, therefore, the oxide layer thickness of the defective rod with the concentrated hydrides as shown in Fig. 1 was compared to those of the intact rod with no concentrated hydrides (Fig. 2). Figs. 6 and 7 show the oxide

layer thickness with the axial elevation for the defective and intact rods, respectively. At the bottom part, both rods showed the similarly thin oxide layer of 5 μm. However, at the upper part of the defective rod where the hydrides were concentrated near the outer cladding surface adjacent to the oxide front, the thick layer of as much as 50 μm was formed (Fig. 6). In contrast, the intact rod with uniform distribution of hydrides had no accelerated corrosion so that the oxide layer at its corresponding upper part was less than 10 μm (Fig. 7). Since the cladding surface temperature is determined by heat transfer coefficient between coolant and cladding and the rod power, we expect both the fuel rods to have the very similar cladding surface temperatures. In addition, the oxide layer thickness of irradiated fuel rods, ranged from 4 to 24 μm at the burnups of 16,000 to 18,000 MWd/MTU as shown in Fig. 8, which is equivalent to the burnups of the defective rod and the intact rod, despite the difference in cladding surface temperatures caused by different power histories [16]. Therefore, we can conclude that the concentrated hydrides accelerate in-reactor corrosion of Zircaloy-4 cladding.

In essence, the results as shown in Figs. 4 and 7 clearly demonstrate that the concentrated hydrides near the oxide/metal interface accelerate out- and in-reactor corrosion of Zircaloy-4 cladding. Conversely, if the hydrides did not become concentrated near the oxide/metal interface, the corrosion acceleration would not occur. To prove this argument, the mini-fuel rods were intentionally subjected to corrosion testing in steam at 400 °C for 150 d, where only the small extent of hydrides was precipitated. As expected, no corrosion acceleration was observed on both tubes as shown in Fig. 9. It is because the extent of hydrides was low and hydrides were very uniformly distributed over the cross-sections of the Zircaloy-4 cladding, as shown in Fig. 10. Consequently, a sufficient condition for the corrosion acceleration is the concentration of hydrides toward the outer cladding surface. This may explain why the pre-hydrided Zircaloy-4 with no concentration of hydrides has shown the similar corrosion behavior to that of unhydrided one as reported by Asher [17] and Knights [18]. Other supportive evidence for the corrosion acceleration was reported by [17]. He reported that the heated Zircaloy-2 with the concentrated hydrides locally at the tube outside had the abnormally thick oxide of 50 to 80 μm, while the unheated control tubes with uniformly distributed hydrides had no accelerated corrosion just with the oxide layer of around 20 μm.

3.3. Accelerated corrosion of Zircaloy-4 cladding at high burnup

The above results demonstrate that in- and out-reactor corrosion of Zircaloy-4 cladding are accelerated by concentrated hydrides on the outer cladding surface adjacent to the oxide front arising from applied circumferential tensile stress. Therefore, accelerated corrosion of intact Zircaloy-4 cladding at high burnup can be explained as the corrosion acceleration by hydrides. At low burnup, the gap between cladding and pellet will not be closed so that Zircaloy-4 cladding will not experience any tensile stress imposed by fuel swelling. Thus, the hydrides have uniform distribution as shown in Fig. 2, so that no corrosion acceleration by the hydrides will take place. With burnup increasing, the gap distance between pellet and cladding will be reduced. Especially, the gap at the three-fourth elevations

would be closed first. Therefore, this part of the cladding will be subjected to the highest tensile stress by fuel swelling because the amount of fuel swelling is the highest at this elevation along with the gap closure. When the applied tensile stress builds up enough, then the hydrides over a cladding cross-section become non-uniformly distributed mainly on the outer cladding surface as shown in Figs. 1 and 3, which will be promoted also by a temperature gradient between the inner and outer surfaces. It is to note that the concentration of hydrides like that, especially on the outer cladding surface, is quite often observed on fuel rods irradiated up to high burnup [1-3]. Therefore, the onset of accelerated corrosion of Zircaloy-4 cladding will depend upon when to have the gap closure and upon the extent of fuel swelling. In addition, at the upper part where the gap closure occurs earlier, the tensile stress imposed by fuel swelling will increase proportionally to the burnup increase. Thus, at high burnup, the imposed tensile stress on the cladding will become so large as to have many hydrides concentrated only on the outer cladding surface. Conclusively, the corrosion acceleration by hydrides will be the largest at the upper part where the gap is closed first as shown by Kilp [19].

4. Conclusion

The simulation study demonstrated that applied tensile stress by fuel swelling causes hydrides to become concentrated on the outer cladding surface through diffusion of hydrogen from the inner surface under compressive stress to the outer surface under tensile stress. Thus, it is concluded that the concentration of hydrides observed only on the defective rod is caused by applied tensile stress by fuel swelling probably due to the higher fuel temperature. However, the concentrated hydrides on the outer cladding surface adjacent to the oxide front led to an acceleration of out- and in-reactor corrosion of Zircaloy-4 cladding. Consequently, the accelerated corrosion of Zircaloy-4 cladding at high burnup in light water reactors is suggested to arise from the concentration of hydrides near the outer surface that occurs at high burnup due to the increased tensile stress by fuel swelling.

Acknowledgment

5. References

[1] T. D. Pyecha, G. M. Bain, W. A. McInteer, and C. H. Pham, Proceedings of ANS Topical Meeting on LWR Water Reactor Fuel Performance (1985) p. 3-17.

[2] P. Guedeny, M. Trotabas and M. Boschiero, Proceedings of ANS-ENS International Conference on Light Water Reactor Fuel Performance (1991) p. 627.

[3] A. M. Garde, Proc. 9th Int. Symp. on Zirconium in the Nuclear Industry, ASTM STP 1132 (1991) p.

566.

[4] Y. S. Kim and Y. H. Koo, KAERI Report, Korea Atomic Energy Research Institute, TR-FM-KR1-91002, August 1991.

[5] D. O. Pickman, Studsvik Report, Studsvik, STUDSVIK/NF(R)-89/83, 1989.

[6] B. J. Lewis, Proceedings of Int. Topical Meeting on LWR Fuel Performance (1988) pp. 165.

[7] Y. S. Kim, K. S. Rheem and D. K. Min, Proc. 10th Int. Symp. on Zirconium in the Nuclear Industry, American Society for Testing and Materials, ASTM STP 1245 (1994) p. 745.

[8] M. R. Louthan, Jr. and R. P. Marshall, J. Nucl. Mater. 9 (1963) 170.

[9] P. Efsing and K. Pettersson, Proc. 11th Int. Symp. on Zirconium in the Nuclear Industry, ASTM STP 1295 (1996) p. 394.

[10] R. Dutton, K. Nuttal, M. P. Puls and L. A. Simpson, Met. Trans. 8A (1977) 1553.

[11] K. Nuttal and A. J. Rogowski, J. Nucl. Mater. 80 (1979) 279.

[12] R. L. Eadie and C. E. Coleman, Scripta metall. 23 (1989) 1865.

[13] C. E. Coleman and J. F. R. Ambler, Proc. 3rd Int. Symp. on Zirconium in the Nuclear Industry, ASTM STP 633, (1977) p. 589.

[14] Y. S. Kim. S. M. Seon, S. S. Kim and S. I. Kwon, J. Korean Inst. Met. & Mater. (1999) in progress.

[15] S. Persson, A. R. Massih, G. Frenning, R. Lunabba, Proceedings of ANS-ENS International Conference on Light Water Reactor Fuel Performance (1991) p. 549.

[16] S. G. Noh, KAERI Report, Korea Atomic Energy Research Institute, KAERI/RR-1024/91, 1991.

[17] R. C. Asher, and F. C. Trowse, J. Nucl. Mater. 35 (1970) 115.

[18] C. F. Knights and R. J. Perkins, J. Nucl. Mater. 36 (1970) 180.

[19] G. R. Kilp, M. G. Balfour, R. N. Stanutz, K. R. McAtee, R. S. Miller, L. H. Boman, N. P. Wolfhope, O. Ozer and R. L. Yang, Proceedings of ANS-ENS International Conference on Light Water Reactor Fuel Performance (1991) p. 730.
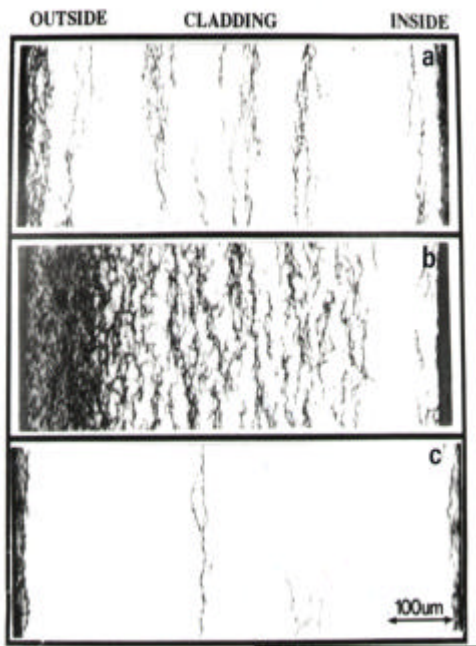
Fig.1. Distribution of hydrides on the defective rod irradiated for 2 cycles at the axial elevations of: (1) 3592 mm, (b) 2902 mm and (c) 655 mm.
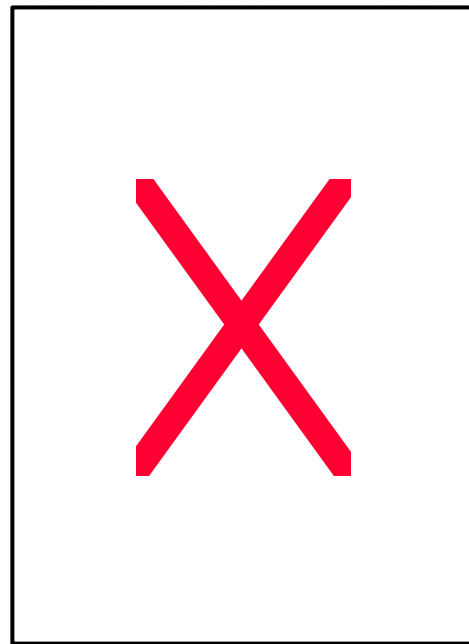

Fig.2. Distribution of hydrides on an intact rod next the defective one with the same power history at the axial elevations of: (1) 3500 mm, (b) 3200mm and (c) 350 mm.
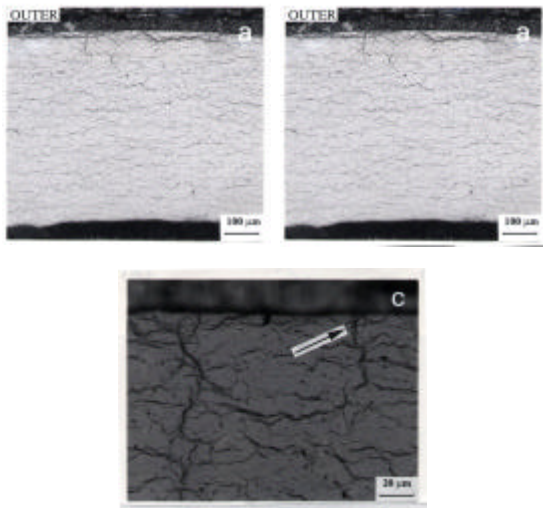

Fig. 3. Concentration of hydrides on (a) the stressed Zircaloy-4 cladding tube as opposed to the uniform distribution of hydrides on (b) the unstressed one and (c) the radial hydrides near the outer surface of the stressed one after corrosion in LiOH solution with 2200 ppm Li for 4 d.
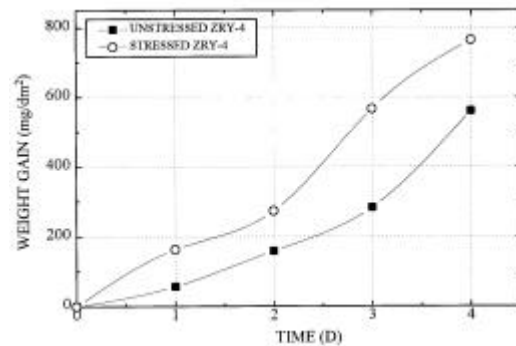
Fig. 4. Change of weight gains with time of the stressed and unstressed Zircaloy-4 cladding tubes in LiOH solution with 2200 ppm Li at 350 ºC
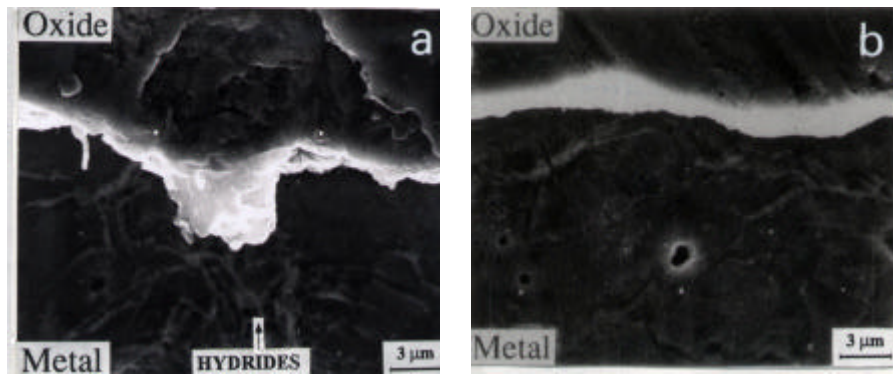
Fig. 5. Enlarged oxide/metal interface boundaries of (a) stressed Zircaloy-4 cladding tube and (b) the unstressed one after corrosion in LiOH solution containing 2200 ppm Li at 350 °C for 4d
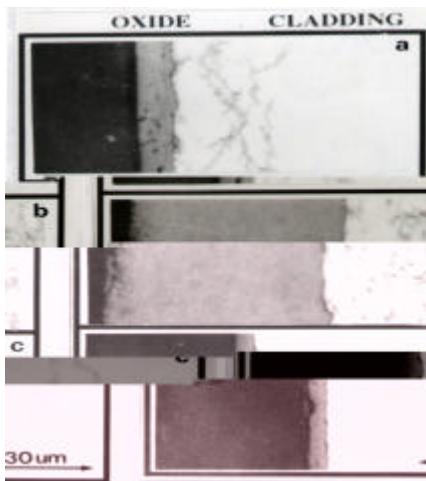

Fig. 6. Oxide layer thickness of the defective rod at the axial elevations of (a) 3592 mm and (b) 2902 mm and (c) 655 mm.
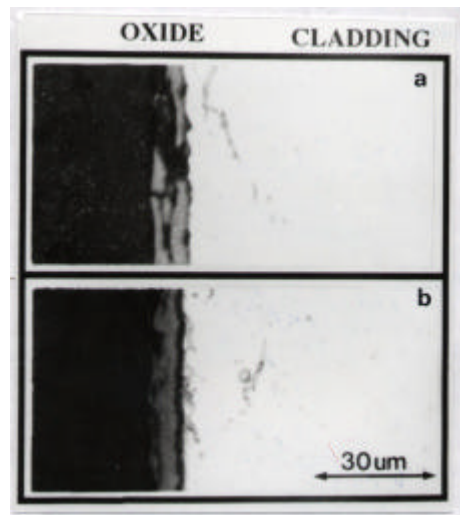

Fig.7. Oxide layer thickness of the intact rod at the axial elevations of (a) 3174 mm and (b) 2104 mm.
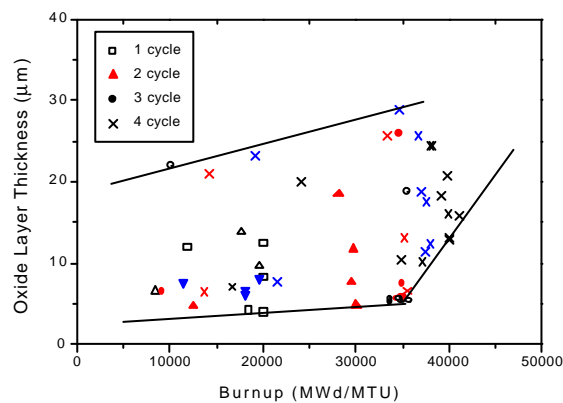

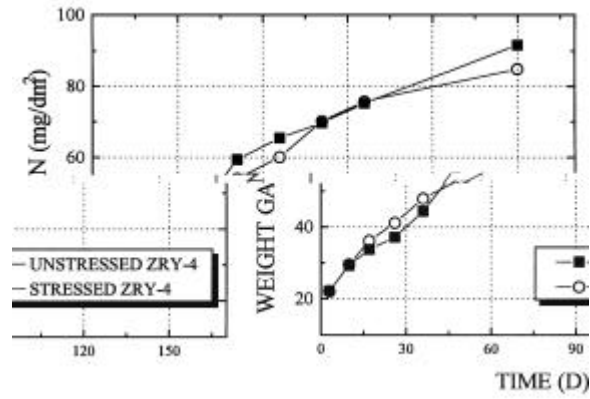Fig. 8. Change of the oxide layer thickness with burnup on the fuel rods with 1 to 4 cycle irradiation

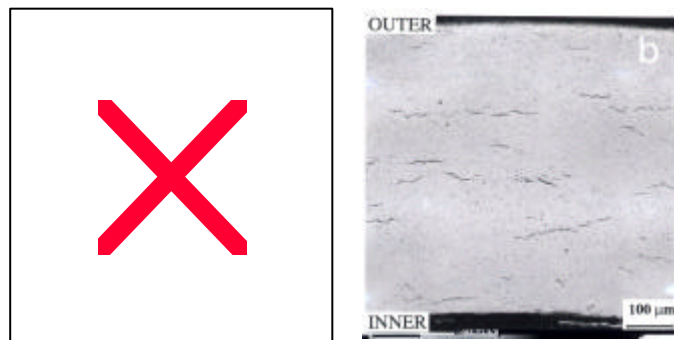Fig. 9. Corrosion of stressed Zircaloy-4 cladding and the unstressed one in steam at 400 ºC

Fig. 10. Uniform hydride distribution of (a) unstressed Zircaloy-4 cladding and (b) the unstressed one after corrosion in steam at 400 ºC for 150 d