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# ADVANCES IN THE UNDERSTANDING OF THE MECHANISMS OF IODINE-INDUCED SCC CRACKING IN ZIRCONIUM ALLOYS

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## ABSTRACT

In pressurized water reactors (PWR) the fuel rod cladding is the first barrier against the spread of fission products. It is therefore essential to guarantee its use in the reactor. Sometimes the production of electricity requires that certain power plants operate in "network monitoring". The fuel introduced into nuclear power reactors can then undergo sometimes significant power variations. Following a severe reactor power transient, clad failure can occur through a stress corrosion phenomenon (SCC), under the combined action of mechanical stresses and gaseous fission products generated by the fuel pellets. Among those iodine plays a major role, for it may induce SCC in zircaloy. In the early ages of water-cooled reactors (PWRs, BWRs or CANDU), series of similar failures took place following sharp startups. Today power increase rates as well as instantaneous local power levels are limited. Indeed, it is well know that cladding failure by iodine-induced stress corrosion cracking (I-SCC) may occur under pellet-cladding interactions (PCI) conditions during power transients in PWRs. In this paper we review the advances in the understanding of these SCC cracking mechanisms of the fuel rod cladding that would then allow better control of the integrity of the clad during the more severe demands related to the operating conditions of the PWRs.

## 1. INTRODUCTION

The lifetime of a nuclear power reactor depends on the properties of the materials involved in its structure. However, the environment generated in the operating conditions of these reactors can accelerate the process of degradation of these materials and should be the object of systematic studies, not only to preserve their specificities but also the capacity to increase their lifetime in operation.

One of the main phenomena that occur in reactors due to the fission products generated during operation is stress corrosion cracking (SCC), where the corrosive environment and the presence of cracks under stress can lead to an early embrittlement of the materials. In fuel cladding, fracture by embrittlement occurs mainly through the action of iodine, inducing microcracks (ISCC) in the grain boundaries, which coalesce, grow and propagate leading to failure by cracking, which are justified by the favorable conditions found in the operating environment of the reactor.

In this work, a review of the studies on this phenomenon will be presented, for a better understanding of the mechanisms that allow the I-SCC and the factors that can accelerate its process.

## 2. I-SCC IN ZIRCONIUM ALLOYS

Work by Goryachev et al. [1] employed Zr and several of its alloys to compare the susceptibility to SCC in flowing iodine vapor at a constant strain rate. The tests were performed using flat cladding samples of Zr and its alloy as well as Zr coated Zr-1% Nb. Although all the alloys are prone to SCC, it is possible to determine which materials with higher ductility and lower strength present a higher resistance to SCC than the less plastic ones, but with greater strength. Thus Zr is more resistant to SCC than Zry-4.

The analyzed alloys presented a susceptibility to SCC at a constant strain rate, among which Zr-1% Nb presented the highest resistance. Many are the factors that determine this result, but according to the author the texture of the cladding is what most affects the resistance to SCC. Iodine inducing cracking is observed only in the direction of tangential stress where the texture parameters are greater than 0.1. Thus, the radial texture formation in the cladding would be an efficient method of protection against SCC.

The variables that most influence SCC in Zr-1% Nb cladding loaded in the tangential direction, are: temperature, deformation ratio and partial pressure of iodine. Thus, at the strain rate of $2 \times 10^{-5}\ s^{-1}$ and 350°C the critical iodine partial pressure was 500 MPa, whereas at the same temperature, with a partial pressure of 900 Pa, the critical strain rate was $5 \times 10^{-5}\ s^{-1}$ . At the strain rate of $2 \times 10^{-5}\ s^{-1}$ the iodine partial pressure of 900 Pa Scc was observed at the temperature range 200-400 ° C.

After a review on the subject, Nikulin et al. [2] summarizes the effects of external factors, structures and properties of zirconium alloys on the influence on SCC of the fuel element cladding. According to them, the chemical composition is the main influence factor in SCC, being responsible for changes in the structure, phase composition and mechanical and physical properties of the alloys. The result of this influence hinders the individual evaluation of each factor, making it very imprecise the comparison between SCC results in cladding manufactured with different alloys. However, the result of most studies shows that changes in chemical composition affect the resistance of the cladding to SCCs primarily through the change in their strength.

According to the authors, the influence of the texture to SCC occurs by the propagation of intragrade corrosion cracks on the basal planes of the zirconium matrix. The propagation ratio of intragranular cracks is two orders of magnitude larger than the intergranular propagation, being determinant for the time before failure. The structure of the alloys and the condition of the cladding surface produces a much weaker effect in SCC, being important only in the initial stages of the fracture. Increasing the temperature of the corrosive medium decreases the resistance of the zirconium cladding to SCC and this increase may change the corrosion cracking mechanism.

Irradiation does not change the mechanism of SCC in zirconium cladding, being observed in different works in the literature that changes occur between before and after irradiation, by means of internal factors. Zircaloy becomes sensitive to SCC after irradiation with fluxes exceeding $2.1 \times 10^{20}$ n / cm $^2$ and are not sensitive to fluxes around $8 \times 10^{19}$ n / cm $^2$.

The type of particle present in the alloy may influence the initial stage of cracking in SCC, and the particles containing iron in zirconium alloys are considered as catalysts.

In summary, the SCC resistance of the nuclear fuel cladding made from zirconium alloys in iodine-containing medium decreases with increasing external loading, temperature, iodine concentration in the medium and the value of irradiation dose. The highest resistance to SCC will be obtained with cladding of high purity surface made of lower strength alloys that have a highly recrystallized structure with uniform distribution of second phase particles and presenting a radial texture.

## 3. MECHANISMS OF SCC

Some models have been postulated to explain the onset and growth of crack up to fracture failure. Localized microvoid coalescence model is also proposed by several authors, but no evidence of micro-ductility found on fracture surfaces. In addition, some authors associate pre-existing defects with origin and beginning of cracks in claddings.

According to Park et al. [3], researchers have failed to reach a consensus on crack nucleation, not to mention the intergranular (IG) or transgranular (TG) nature of the beginning of the crack. Recently, two models were proposed to explain the nucleation and growth of crack in the cladding: the grain boundary pitting coalescence model (GBPC) and the pitting assisted slip cleavage (PASC) model. In order to verify these models, I-SCC (iodine-induced stress corrosion crack) tests were done on zirconium alloys.

The results of the time to rupture and crack propagation tests performed on Zry-4 and Zr-Nb claddings show that the factors that most affect crack initiation are nucleation of pitting, growth and agglomeration at the GB, which increase with iodine concentration and the hoop stress. The GB pits are the result of a series of reactions, beginning with the weakening of Zr-Zr bonds by iodine adsorption, $ZrI_4$ gas formation and separation from the GB, regeneration of active iodine by thermal decomposition of $ZrI_4$. The pits preferably form along the GBs because the GB is rendered brittle by an impurity or weaker by the slip band.

A cleavage crack is generated to a certain extent when pits are combined in the crystallographic slip plane as indicated by the PASC model and the crack propagation ratio also increases. Above the $K_{ISCC}$ value a microcrack grows mainly due to GBPC and above that value it spreads rapidly due to PASC. The initial crack in the GBPC model is mainly affected by grain size and orientation, rather than by a micro-failure mechanism.

The addition of Nb increases the resistance to pitting generation and is associated with agglomeration. Thus, the cladding containing Nb has a higher $K_{ISCC}$ value and a crack propagation ratio lower than that of zircaloy-4.

Tests performed on zircaloy-4 claddings, with as received (SR) and recrystallized (RX), microstructures, performed by Park et al. [4] show that when exposed to high temperatures and high-pressure iodine environment, they generate pits preferentially in grain boundaries. These pits will coalesce to form a microcrack to accommodate a position for the crack nucleation, such as the GBPC model. Microcrack can develop into an incipient crack that begins and propagates along the grain boundary. This incipient crack is more evident for the SR structure than for RX due to grain morphology.

Fractographs obtained in this work confirmed the PASC model evidenced through a set of pits generated on the IG crack surface. When combined in the crystallographic sliding plane, a cleavage crack was generated to a certain extent. The iodine effect increased crack propagation velocity by 1000 times while the $K_{ISCC}$ threshold value was decreased by ½ times that of the inert environment.

The SCC mechanism was analyzed by Fregonese et al. [5] and shows that iodine induces SCC failures in zirconium alloys in three steps: (1) the spot of the iodine attack with intergranular development and transgranular propagation before the ductile failure. (2) The proportion of intergranular to transgranular cracking varies depending on the composition of the alloy and the environmental nature of iodine. (3) Transgranular propagation occurs by cleavage-like on basal plane and fluting. It is the result of competition between a plastic accommodation of the applied strain and the brittle fracture. For both intergranular and transgranular cracking, an iodine adsorption mechanism along the crack faces and at crack tip may be involved.

For the development of intergranular cracking, the adsorption can be assisted by both a dissolution mechanism and by the formation of zirconium iodide. On the other hand, for transgranular cracking, some calculations confirmed by ab-initio modeling show that iodine adsorption leads to a reduction of Gibbs surface energy, which affects the basal plane preferentially. In general, the crack velocity depends on environmental parameters such as electrochemical potential, nature and concentration or partial pressure of chemical species and temperature. Metallurgically depends on the alloy composition, texture and flow and on mechanical parameters such as nature, level and orientation of applied stress, stress intensity factor and strain ratio. The texture seems to be the control parameter of transgranular cracking of unirradiated zircaloy-4.

The results on strain-hardening influence using acoustic emission, proposed by Fregonese, show the occurrence of an adsorption-dissolution mechanism for intergranular development, while transgranular cracking involves brittle fracture of compact crystallographic planes combined with plastic deformation. It has also been shown that strain-hardening increases the transgranular propagation of SCC cracks.

Although the contribution of the twins is limited, the influence of strain-hardening is linked to the activation of prismatic slip. If no strain localization within grains can be responsible for transgranular cracking enhancement, strain incompatibilities between grains can be considered to account for pseudo-cleavage activation on strain-hardening zircaloy-4; they act to favor transgranular initiation at coarse slip bands and grains boundaries intersections and in increasing the internal stress component of flow stress.

Park et al. [6] carried out a study in zircaloy-4 and Zirlo, to analyze the validity of GBPC and PASC models, considering the effect of microstructure and an alloying element on transgranular (TG) cracking by PASC model. According to them, these models explain very well the ISCC behavior in terms of nucleation, initiation and propagation of crack in the zircaloy-4 or Zirlo claddings in iodine environment.

When a crack reaches a threshold value $K_{ISCC}$ it propagates fast and this fact reveals that the grain shape and the cleavage habit plane play an important role in a grain cracking by GB pitting, which results in the IG-$TG_C$ (often occurs in a recrystallized structure) or $TG_f$-$TG_c$ (appears frequently which increase the propagation rate) cracking mode. An increase in pit resistance in a grain boundary plays a critical role in decreasing the crack propagation ratio of the Zirlo cladding.

A study of zircaloy-4 irradiated by proton, performed by Fournier et al. [7] shows the same changes as those produced with neutron. In $Zr(Fe, Cr)_2$ precipitates amorphization or Fe redistribution were observed after irradiation. Finite element calculations suggest that 0.5% macroscopic strain corresponds to 70% of the yield stress of the irradiated material in the proton-irradiated layer. Analysis shows that irradiation induces a change in slip system activation from prismatic to basal via a change in the hierarchy of critical shear stress.

When analyzing zirconium fuel element rods Nikulin et al. [8] finds that even with different compositions, the sequence of processes for I-SCC is identical for all the alloys: dissolution of the oxidized film and erosion away from the surface of the tube, formation and development of pitting and finally generation and growth of cracks in surface pits of and internal cracks. The strength of the tubes controls the attainment of some mechanisms and kinetics of failures. An increase in alloy yield strength from 340 to 580 MPa leads to a reduction in the time to failure by a factor of 3.6 predominantly as a result of an increase in crack formation in tubes.

The content of impurities, the type of matrix microstructure and the number of second-phase particles govern the residual ductility of oxidized zirconium fuel rods made of alloy. These results are important for the development and certification of new modifications of zirconium alloys aimed at the operation of a new generation of power reactor.

Lewis et al. [9] have done a thermodynamic analysis to study the I-SCC phenomenon for fuel cladding of CANDU type reactors, developing a mechanistic kinetic model of its own. In this model were incorporated the diffusion of fission products, $I_2$ vapor transport in the fuel-clad gap and crack propagation by ZrI4 production. Although the result is in good agreement with the experimental observations, its validation requires experiments in reactor power ramp.

New insights about the phenomenon of ISCC in zirconium alloys is presented by Gillen et al. [10] through advanced 3D techniques compared to the already well-established 2D techniques. The use of 3D characterization techniques reveals the complex nature of the ISCC cracks and shows the importance of using multiscales to friable the propagation of cracks. This study is based on observations of morphology of cracks in recrystallized and cold worked materials. Through the R-X computed tomography (XCT) technique it is possible to observe a finger-like crack branches in front of the primary crack. These microbranches are observed in the extension in finer structures through the 3D-EBSD technique with different results for the recrystallized and cold worked situations.

By performing a serial sectioning, it is possible to investigate the interaction between the crack tip and the local microstructure, on a finer scale, with the disclosure of details of the crack beyond the resolution of XCT and crucially giving access to the full five parameters of grain boundary description. For the first time it was possible to show the segregation of iodine ahead of the crack tip using high resolution 3D chemical analysis.

During investigation of irradiated and non-irradiated zirconium alloys conducted by Gillen et al. [11] it is possible to observe a possible preference for non-basal transgranular cracking in the tested neutron irradiated mandrel material. Although with different compositions and loading geometry, different morphologies and orientation dependence are more likely due to irradiation and corrosive environment. Irradiation increases the slippage activity in prismatic and pyramidal planes allowing for fluting between cleavage planes, which are possible conditions in non-irradiated materials.

Stress localization due to irradiation-induced dislocation channeling and the resulting loss of ductility may increase I-SCC susceptibility further. Ample understanding about the aspects at the tip of the crack formed by the different alloys will be possible with the use of the techniques presented in this study.

## 4. CONCLUSIONS

The study of the phenomenon of I-SCC in zirconium alloys, that occurs in pressurized water reactors, shows to the present day a good understanding of the necessary steps for its nucleation and evolution. The influence of parameters in this process such as alloy chemical composition, claddings texture, temperature, irradiation flux, iodine partial pressure, etc., are widely studied mainly by the individual variation of each factor. However, I-SCC is a phenomenon that occurs due to the interdependence of three factors: corrosive environment, applied stress and susceptible material, which turns very complex the reproduction of the conditions that lead to the understanding of the phenomenon as a whole. The GBPC (Grain Boundary Pitting Coalescence) and PASC (Pitting Assisted Slip Cleavage) models are tools that attempt to explain the phenomena of crack nucleation and growth in claddings.

The new multiscale and 3D conditions observation techniques promise to be the sources of better understanding of details and development processes of I-SCC in zirconium alloys. This study is of fundamental importance for the development of new alloys, which will allow an increase in reactor life.

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