



Deformation–corrosion interactions for Zr alloys during I-SCC crack initiation

Part I: Chemical contributions

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Abstract

For a better understanding of the initiation step of iodine-induced stress corrosion cracking in Zr alloys, responsible for pellet–cladding interaction (PCI) fuel rod failures, an analytical study has been undertaken, the aim of which being focused on the respective roles of local chemistry and stress/strain state on the crack nucleation. This first part is mostly related to the chemical environment. From the tensile tests performed under iodine rich and inert environments, it was concluded that no crack initiation could be detected following the tests in an inert atmosphere. The iodine induced stress corrosion initiation mechanism must therefore be analysed as a corrosion–strain interaction. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

In certain countries, where a major proportion of the electricity produced is of nuclear origin and where the electricity production network must be capable of adapting to consumption demand, it is absolutely essential to have strict control of the physico-chemical processes influencing the integrity of the fuel rod cladding on the occasion of induced local power variations responsible for a pellet–cladding interaction (PCI) phenomenon. Under transient power conditions, it has been observed that this phenomenon leads to high-pressure contact between cladding and fuel inducing first elastic, and subsequently plastic, strain of the cladding up to a value of 0.5–1% [1]. The presence of corrosive fission products, including iodine, may activate a stress–corrosion cracking (SCC) process of the cladding material [2–4]. From the study of failure surfaces obtained by SCC

of Zircaloy-4 in a variety of chemical environments, it was concluded that iodine is responsible for cladding failures during power ramps [2,5,6]. Moreover, it is clear that the radiolysis effects of the fission products and the gamma radiation lead to the creation of a sufficient quantity of free iodine to cause SCC of Zircaloy [7].

Cladding failure by iodine-induced SCC can be described in four stages [8–11]:

- crack initiation,
- localised growth (intergranular),
- transgranular propagation,
- final cladding failure by plastic instability and ductile tearing.

The crack propagation stage commences when the stress intensity factor at the root of the crack reaches a threshold value K_{I-SCC} [10–12]. This results from two opposing phenomena, namely pseudo-cleavage failure (chemically assisted cleavage) which occurs on a basal plane of the compact hexagonal lattice of the zirconium, and failure giving rise to fluting as a result of strain on the prismatic planes of the hexagonal lattice. This combination of opposing phenomena explains why texture is the predominant metallurgical factor governing the lifetime of the material subjected to iodine-induced SCC [12,13].

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However, the first two stages, although potentially a large part of the lifetime of cladding material subjected to PCI, are nonetheless still far from being clearly understood [14]. Depending on whether the chemical effects or the mechanical effects are considered to be dominant in the crack initiation stage, this stage is described as an oxide layer degradation phase [8,9], an iodine interaction localisation phase [14], or as the stage that is not governed by stress singularities [15].

Indeed this stage is sometimes divided into an incubation phase and a defect growth phase [4]. Concerning the location of crack initiation, apart from the possible contribution of pits, hydrides, inclusions or precipitates [16–18], there are still considerable differences of opinion as to whether the process is intergranular or transgranular [2,19–21].

The first part of this study is therefore aimed at specifying the respective roles played by the mechanical and chemical factors in the crack initiation mechanism, based on a determination of the initiation conditions and morphological properties. In a second part [22], the study will be focused more particularly on determining whether the fundamental role played by material crystallography and grain orientation in stress–corrosion crack propagation lies at the crack initiation stage. Following this, a discussion will be made on the localisation of the initial cracks at a microstructural scale.

2. Conventional approach to stress–corrosion cracking

It is always possible to consider the existence of an initial defect, scratch or pit, as a basis for reasoning the point of departure of a micro-crack and subsequently build a stress–corrosion crack propagation model. However, the microscopic mechanisms driving crack growth are not necessarily very different from those leading to the creation of the initial defect. It would therefore seem pertinent to briefly review the various descriptions of stress–corrosion cracking.

Historically, an electrochemical approach to SCC phenomena came first of all: prevalence was given to a process linked to localised corrosion mechanisms, with gradual introduction of the effects of local strain at the bottom of the crack. More recently, in addition to making allowance for the role of hydrogen, attempts were made to integrate the dual corrosion–strain function and models were introduced in which plasticity plays a more important role through its interactions with electrochemical mechanisms.

Most of the models attribute a predominant role to the failure of the protective film, covering the mechanical, chemical and electrochemical effects, generally considering that mechanical failure of the passive film occurs at slip or twin emergence points. In the

anodic dissolution model, this phenomenon is considered overall with the concept of critical strain required for film failure: ϵ_f . In this way, destabilisation of the protective film can be explained by the corrosive atmosphere [23,24], with subsequent non-reconstitution and/or its transformation into a non-protective film [25–27].

Crack formation or propagation can then itself result from different mechanisms. In aluminium or steel alloys, cracks are generally linked to the existence of an intergranular anodic path, possibly assisted by strain [28]. In copper alloys, the mechanism involves fast propagation of a cleavage crack formed in the porous film, created on the surface by selective dissolution [27]. In other cases, the production of vacancies or dislocations following localised anodic dissolution, promotes crack formation [29]. Finally, hydrogen may play a role by locally reducing the inter-atomic cohesion forces (by adsorption), by interacting with the dislocations, by promoting the formation of micro-cavities or by forming brittle hydrides locally [30].

In the case of the Zr-iodine system, electrochemical models are generally discarded because of the molecular nature of the iodine present in the pellet–cladding gap. Moreover, hydrogen, in hydride form, is considered to be responsible for a deferred failure mechanism which, according to fracture micrographic studies, would not play any part in the iodine-induced SCC mechanism [9]. Conversely, hydrides can serve as crack initiation sites [31]. A weakening of the Zr–Zr links is considered, coupled with a reduction in surface energy, due to iodine adsorption [6,32–35]. In addition, the free iodine can react with the zirconium to form solid iodides and a gaseous zirconium tetra-iodide [16].

From a mechanical standpoint, once a stress threshold has been reached, this could prevail [4,8]; however, many authors consider that macroscopic stress is not as important as the resolved stress on the base plane [36] or the microscopic stress appearing in the vicinity of precipitates or inclusions [16–18] or resulting from grain-to-grain strain incompatibilities [18].

The wide range of hypotheses proposed therefore clearly indicates that there is no consensus on the microstructural location, nor even on the intergranular or transgranular nature of crack initiation [19,20,37]. This study is aimed at obtaining a better understanding of the chemical and mechanical contributions in stress–corrosion crack initiation in Zr alloys in the presence of iodine.

3. Experimental techniques

Slow tensile tests were carried out to quantify the conditions under which stress–corrosion cracks appear. Although this is not exactly a pure crack initiation test,

it nonetheless allows the stress applied to the material and its strain to be controlled. To understand more clearly the role of plasticity in crack initiation, some tensile tests were interrupted for intermediate observations.

The materials studied were as follows:

- Two sheets of zirconium (Z1 and Z2) of 1.3 and 0.8 mm thickness respectively and about 25 μm grain size. Their compositions are given in Table 1. The $\{0002\}$ pole figures give an average value of the angle ϕ^* , between the axis $\langle c \rangle$ and the normal to the sheet, of 0° for Z1 and 24° for Z2.
- A Zircaloy-4 sheet (Zry-4), 0.6 mm thick, with an approximate grain size of 8 μm and with a composition as given in Table 1. The angle ϕ^* characterising its texture is 18° . The Zry-4 and Z2 sheets have comparable textures.

With a view to increasing the grain size, certain samples were annealed at 780°C under secondary vacuum. Grain size then reached 250 μm for the Zr sheets, and 500 μm for the Zry-4. All the test specimens were cut from the sheet in the transverse direction, corresponding to a high SCC susceptibility. They have an effective length of 5 mm. After electrolytic polishing, a grid pattern (250 $\mu\text{m} \times 500 \mu\text{m}$) is engraved on the surface of the test specimens using the diamond point of a micro-hardness tester. This geometrical reference frame is also used to determine local strain of the material after tensile testing. Indeed, in this study the term “local strain” is defined as the tensile strain measured with one grid cell, along the tensile direction. The “local” strain gauge is therefore of a length of 500 μm .

The tests were conducted in two different atmospheres: first in iodine vapour at 350°C (mixture of argon and iodine vapour) generally chosen as being representative of reactor conditions and, secondly, in iodine-rich methanol at ambient temperature, which is easier to handle and gives the same fracture surfaces as the tests in iodine vapour.

The tensile testing device consists of a servo-mechanical tensile machine controlled by a function generator. A cross head speed of 5 mm/min was adopted, corresponding to a strain rate of $1.5 \times 10^{-6} \text{ s}^{-1}$.

For the tests in iodine vapour atmosphere, a silica tube sealed under primary vacuum with the charge of crystallised iodine is placed in the testing chamber. After

pumping, the container is subjected to a slight overpressure of argon, then isolated from the exterior before the temperature is raised. The silica tube is broken mechanically by means of a mechanism activated by the displacement of a cross head. The iodine partial pressure is estimated to be that corresponding to saturation at 350°C (1300 Pa). Tensile tests at ambient temperature were carried out in fresh solutions of iodine in methanol, to avoid the intake of atmospheric humidity.

To quantify the crack density after SCC tests, the test specimens are ultrasonically cleaned in acetone and their external surfaces are observed with an optical microscope or a scanning electron microscope. In addition, some localised X-ray analyses were carried out by means of an EDS system.

4. Experimental results

In order to separate the chemical effects related to the corrosive environment from the mechanical effects, the observations made after testing in a iodine-rich atmosphere were systematically compared with the observations made in an inert atmosphere. The combined effects of temperature and nature of the chemical environment, likely to provide information on the role of iodine in crack initiation, are then taken into account by comparison of tests in iodated methanol at 20°C and tests in iodine vapour at 350°C .

4.1. Slow tensile tests at high temperature

4.1.1. Inert atmosphere at 350°C

All the test specimens have the same macroscopic behaviour with regard to strain behaviour. At the surface, one or two slip systems are observed for each grain with the traces being oriented, as expected, by about 45° with respect to the tensile axis. From the interrupted tensile tests it was noted that, in general, no new slip systems are activated when the strain increases and that only the number and thickness of the slip traces increased. Cross slip was occasionally noted in the vicinity of triple grain boundaries. A high degree of strain heterogeneity was observed, not only from one grain to another (Fig. 1), but also within a given grain: in many cases, one of the two activated directions, near a grain boundary, would appear to respond to the stress induced by the strain of the neighbouring grain more than to the macroscopic tensile stress (Fig. 2). Macroscopic grain boundary sliding was observed (thanks to the network of scratches). From detailed SEM observations, this intergranular slipping was partially attributed to localised strain inside the grain, near the boundary. Finally, it was concluded from a surface examination of the test specimens that no crack initiation occurs at 350°C in an inert atmosphere.

Table 1
Composition of the Zr and Zry-4 sheets used in this study

	Z1 (ppm)	Z2 (ppm)	Zry-4
Sn	<30	<30	1.45%
Fe	480	350	0.21%
Cr	52	29	0.1%
O	720	380	800 ppm

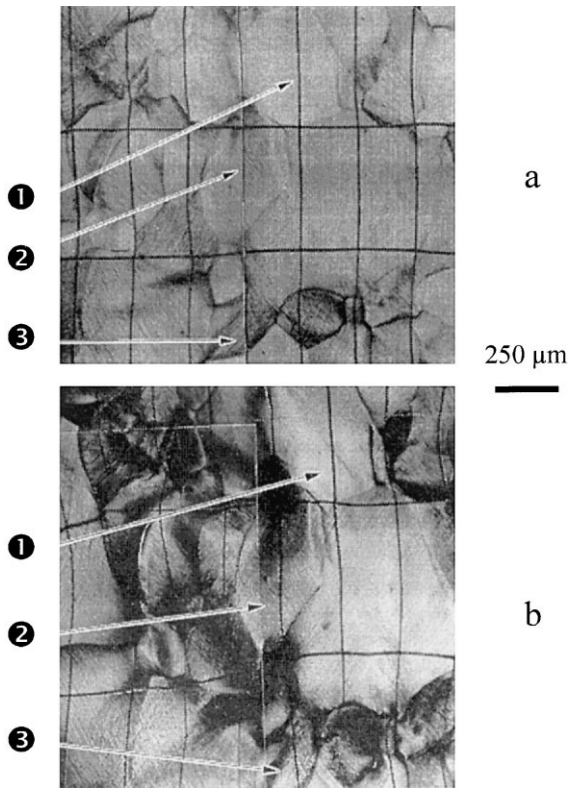


Fig. 1. Slip lines activated during a tensile test at 350°C (Z2) (a) $\epsilon = 4\%$, $\epsilon_{loc} = 5\text{--}10\%$, (b) $\epsilon = 10\%$, $\epsilon_{loc} = 15\text{--}28\%$.

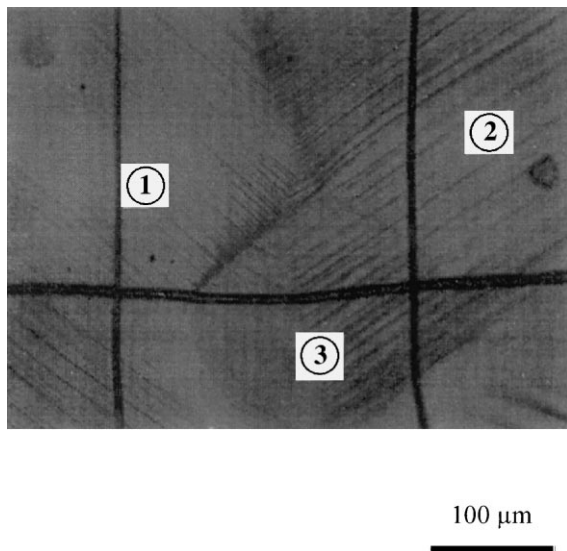


Fig. 2. Heterogeneous strain near grain boundaries (Z1, 350°C, Ar).

4.1.2. Corrosive environment: iodine vapour at 350°C

The macroscopic strain of the materials does not appear to be affected by the corrosive atmosphere: just

as in the inert atmosphere, strain occurs by slipping, with a high degree of heterogeneity from one grain to the next and even within grains.

In all the samples tested, cracks were observed at the surface of the specimens, generally in areas subjected to the highest strain and occasionally accompanied by grain boundary sliding (Fig. 3). The majority of these are intergranular cracks although a few transgranular or composite cracks were detected at the surface of the zirconium test specimens. Numerous cracks are concentrated around triple boundary points where they are sometimes reduced to a simple cavity. Crack size and density were measured in relation to local strain:

- For the zirconium test specimens, the crack length is generally less than the grain size, opening width does not exceed 2–3 μm and the cracks are, on average, arranged perpendicular to the tensile axis. Crack density tends to increase with local strain (Fig. 4).
- The results for Zircaloy-4 test specimens are similar. The average crack length is slightly less than the grain size, opening width is of the order of 1 μm and the cracks are oriented perpendicular to the applied stress direction in general. Crack density also increases with local strain (Fig. 5).

The surface of the samples is highly oxidised. The thickness of the oxide layer would appear to up to several tenths of a micrometer, mainly in the vicinity of slip bands and crack edges; this value is large with respect to the experimental precautions taken and to the temperature holding time of the material at 350°C. Highly oxidised and scaly circular zones were also observed at the surface of certain samples tested in iodine vapour. EDX and SEM analyses detected iodine in all these highly oxidised zones (Fig. 6).

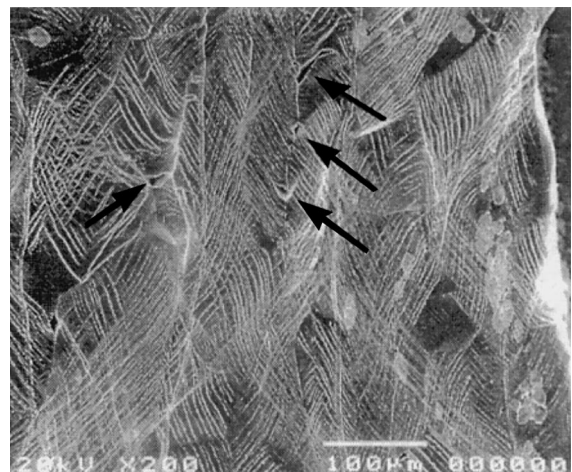


Fig. 3. Intergranular crack initiation in a coarse-grained sample (Z2, 350°C, I₂ vapour).

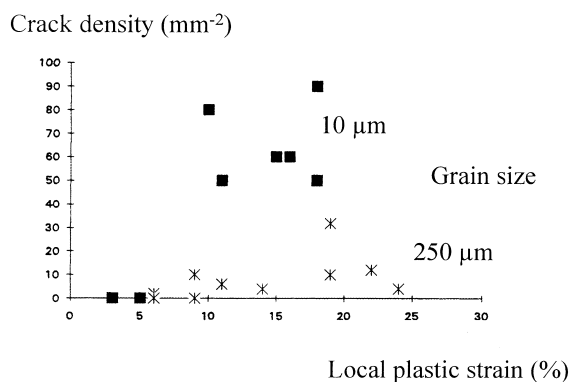


Fig. 4. Influence of local strain on crack density (Z1, 350°C, I₂ vapour).

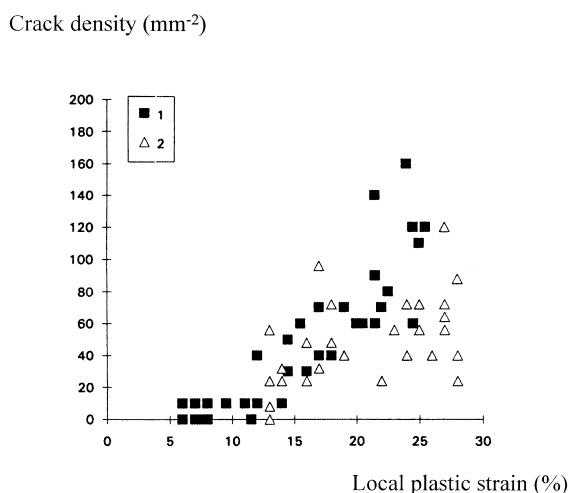


Fig. 5. Influence of local strain on crack density (Zry-4, 350°C, I₂ vapour).

4.2. Behaviour in iodated methanol at ambient temperature

Tensile tests in an inert atmosphere at ambient temperature did not show any sign of crack initiation on the surface of the test specimens. Moreover, it has been shown that pure methanol is innocuous under tensile or maintained stress conditions.

At the surface, polycrystal strain does not appear to differ from that observed in an inert atmosphere (at 350°C or at ambient temperature). In addition, the etch pits obtained at the surface of a specimen showed that the slip bands observed on the surface are compatible with prismatic slip activation.

As with the test in iodine vapour, numerous cracks are observed at the surface of the test specimens. However, the edges of these cracks are generally decorated

with a darker zone, as well as some slip bands (Fig. 7) where EDX and SEM analyses revealed the presence of a considerable amount of oxygen. The cracks are always intergranular. Their size, fairly constant at the surface of a given sample, varies from one specimen to another from a dozen microns to fifty-odd microns; the extent of crack branching and corrosion also varies depending on the specimen. Crack density increases with local strain and iodine concentration in solution (Fig. 8).

5. Analysis of results

Precise definition of crack initiation depends on the sensitivity of the methods used to show up the presence of cracks. The specimens tested in iodated methanol, up to local strains not exceeding 15%, and lightly oxidised, are easy to observe under optical microscopy. The criterion for the existence of a crack is its capacity to be detected at a magnification of 600×. Additional observations by SEM led to the same conclusions.

The specimens tested in iodine vapour are subjected to greater strain and often have a highly oxidised surface. It then becomes necessary to separate metal crack from oxide layer cracking. To determine crack density, cavities measuring several microns were considered. In addition, it should be stressed that the observed cracks, with open edges, necessarily include a mode I opening component. Indeed, even if few grain boundaries are susceptible to shear leading to mode II or III opening, such opening modes would be very difficult to detect, since they would not lead to mouth opening.

Given the intrinsic dual nature of stress corrosion cracking, the results obtained must now be examined from the standpoint of chemical contribution of the corrosive environment, and then with regard to plasticity related to polycrystal strain.

5.1. Chemical role of iodine

Iodine vapour was used, with an estimated iodine partial pressure of 1300 Pa, and also iodated methanol with iodine concentrations of a few ppm (1300 Pa, expressed in terms of number of atoms of iodine per unit volume, is equivalent to an iodine concentration of 40 ppm). For both corrosive atmospheres, the iodine would most likely be present in I₂ form, which is only marginally dissociated into I⁻ ions in methanol. The iodated methanol cannot therefore reasonably be considered as an electrolyte because of its molecular character. Indeed, the work conducted by Elayaperumal [38] has shown that the corrosion rate and time to failure during stress corrosion cracking tests in iodated methanol are independent of the applied electrochemical potential, thus confirming that electrochemical mechanisms of the anodic dissolution type should be discarded.

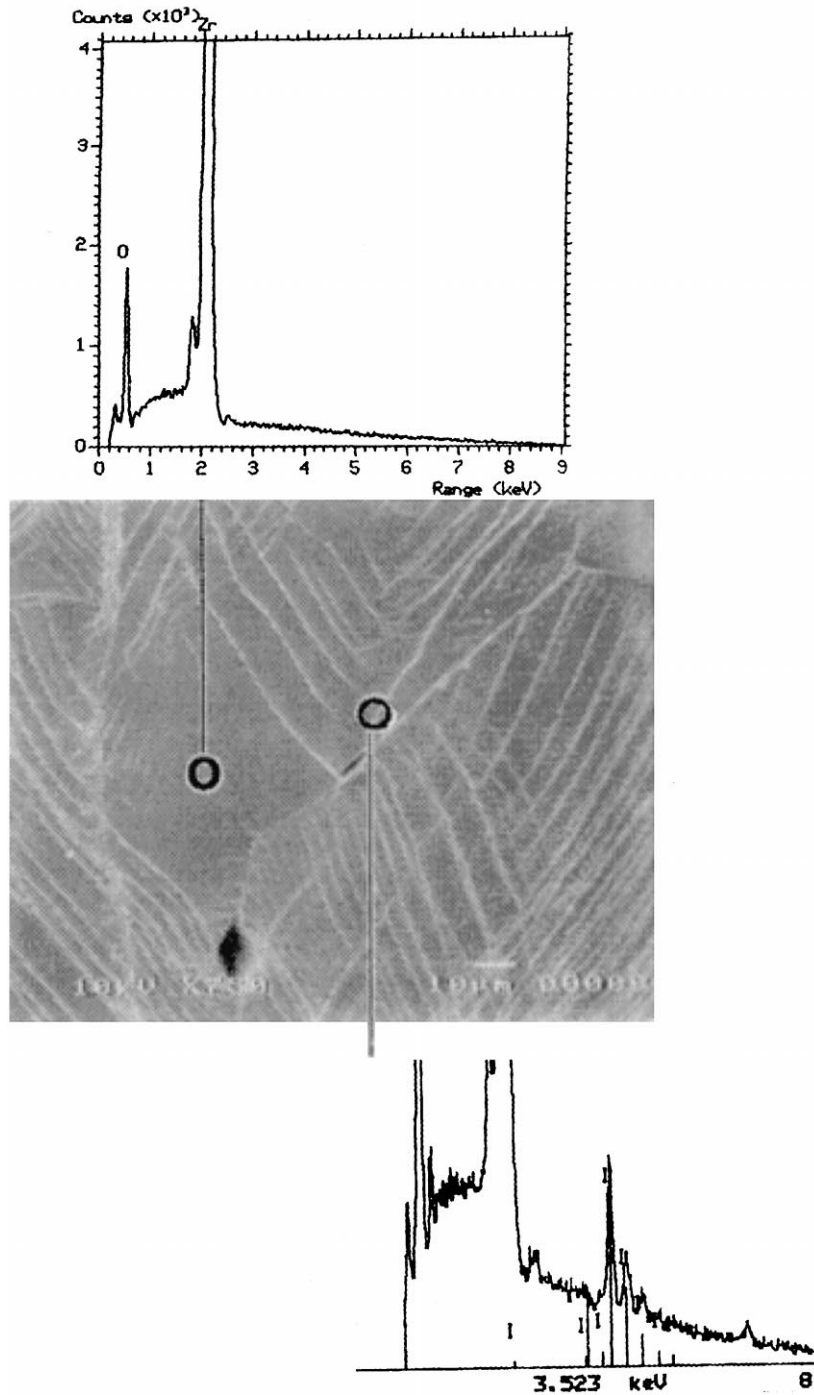


Fig. 6. Preferential iodine localization near a slip band (Z2, 350°C, I₂ vapour).

Some of the experimental results obtained in the present study highlight the role played by iodine with respect to SCC initiation: absence of crack initiations in tests in an inert atmosphere and presence of numerous

intergranular decohesions at the surface of an unstressed zirconium test specimen immersed in a 1% iodated methanol solution for eight days. However, different behaviour patterns were also revealed in relation to the

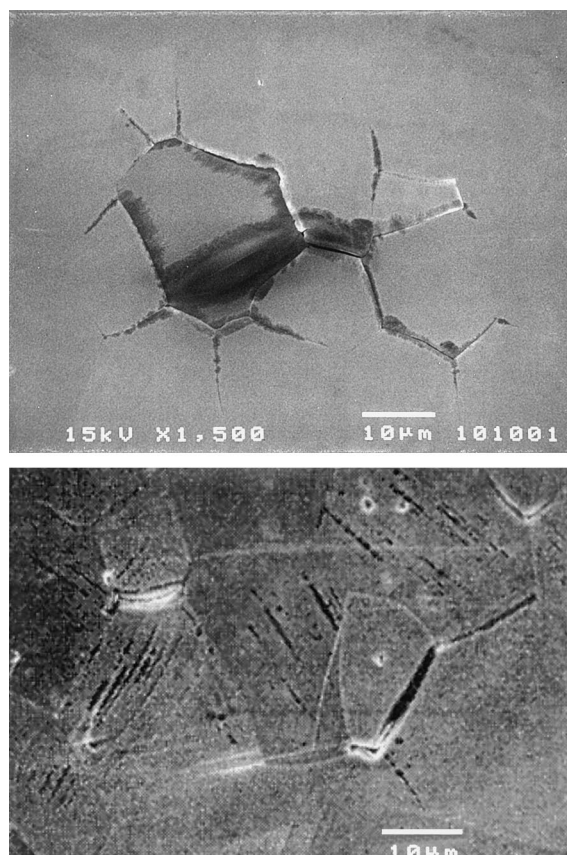


Fig. 7. Intergranular crack initiation and local corrosion in iodated methanol (Z2, ambient temperature, $\text{CH}_3\text{OH} + \text{I}_2$ 1.5 ppm).

corrosive atmosphere chosen. For example, surface oxidation of the material is more pronounced at 350°C. According to Cox and Wood [9], the oxide layer is 5–15 nm thick during tests at room temperature and several tens of nm at 350°C with a vacuum of 10^{-3} mbar. In addition, some transgranular cracks were observed following tests in iodine vapour whereas all the cracks observed during iodated methanol tests are intergranular. This phenomenon may be the result of a competition between iodine and oxygen adsorption at high temperature.

The effect of iodine concentration also appears to be fundamental. For example, for a concentration in excess of 10 ppm, material failure occurs without any generalised plasticity. Since zirconium alloys are easily passivated, this raises the question of what chemical processes might be involved in its depassivation. The destabilisation of a passive film by halogen ions is a known mechanism. For example, pit corrosion of zirconium has been observed in the presence of chloride, bromide and iodide ions as well as in iodine-saturated

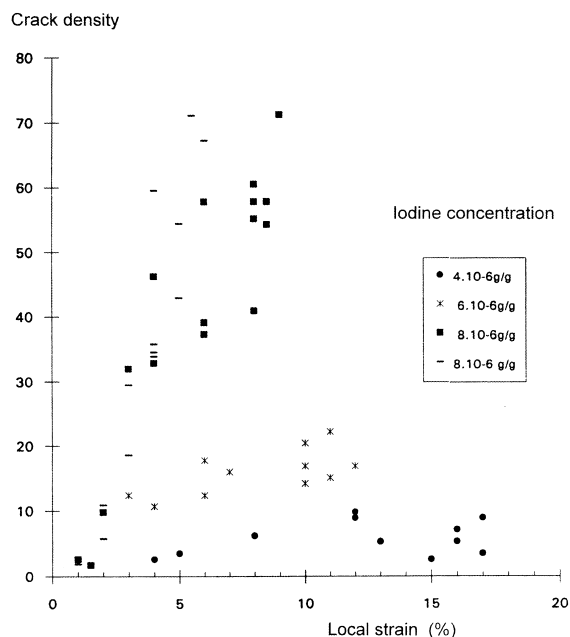


Fig. 8. Influence of local strain and iodine concentration on crack density (Z2, ambient temperature, $\text{CH}_3\text{OH} + \text{I}_2$).

alcohol [39]. In the absence of any mechanical stress and in a liquid environment, three main types of mechanism can be distinguished, which may be involved either separately or jointly in passivation failure [23,24,39]:

- a penetration mechanism (promoted by the disordered structure of the film); despite the fact that the oxide film at the Zircaloy surface seems to be partially amorphous or microcrystallised, the I^- ion would appear to be too large for this process;
- the appearance of mechanical stress: due to the sudden change in the surface potential of the film (excluded by the experimental conditions imposed here) or, what is probably more likely, to the electrostriction mechanism (linked to a change in surface energy of the film following adsorption of I^- ions or I_2 molecules [23]),
- the transfer of metal cations from the internal interface of the film to the electrolyte, thereby leading to thinning and subsequent destruction of the film.

Iodine adsorption at the Zircaloy surface is a mechanism often considered to be the initial mode of action of the iodine. A mechanism based on surface energy modifications, like that proposed by Sato [23], would therefore seem relevant for explaining the destabilisation of the Zircaloy protective film by iodine.

It is also worth adding that the presence of anions can cause a delay in or blocking of the repassivation process [26]. Moreover, the precipitation of metal salts may lead to the formation of a salty film which is no longer protective [40]; this phenomenon could explain

the observed intergranular attack without stress. At the same time, Cox has shown that, on zirconium, a thick porous oxide may form in the presence of an electrolyte containing nitrates, chromates or phosphates [5]. In addition, the growth of an oxide film on the zirconium surface depends on the nature of the electrolyte in which it is grown and the incorporation of anions into the film modifies its electrical properties [41]. This latter point goes in favour of the rupture mechanism by the electrostriction pressure, as envisaged by Sato [23].

The high level of surface oxidation of the test specimens after slow tensile testing in iodine vapour atmosphere and the presence of scaly areas corroborates the theory of loss of zirconium passivity in the presence of iodine. The detection of iodine in the most oxidised areas can be interpreted as being either representative of the formation of a (thick) salty film containing iodine, or indicative of a porous oxide layer with trapped iodine (which comes closer to the work conducted by Cox). Note that the slow tensile tests in iodated methanol, in a similar manner, revealed a locally high level of oxidation which would only be possible in the absence of a protective film.

The preceding analysis does not explain the preferential intergranular cracking observed, even though the passive film is often considered to be finer and more fragile over grain boundaries. It is therefore necessary to consider an intergranular corrosion effect:

- The most usual effect implies a specific chemical composition at grain boundary level. Despite the fact that no intergranular segregation has ever been observed, either in Zircaloy-4 or in zirconium, and that the precipitates are uniformly distributed both across and between grains, grain boundaries without segregation cannot be considered a possibility and, moreover, localised corrosion phenomena are highly sensitive to chemical composition at the interfaces. Regardless of how weak it may be, this effect cannot be excluded from the explanation of the observations made.
- The second effect is a structural effect inherent to the disordered crystallographic character of the grain boundaries, making metal–metal bonds weaker. For example, refined aluminium placed in pressurised water at 150°C is subject to intergranular attack which is all the greater as its purity increases. This spectacular effect in the case of pure aluminium could also be taken into account to interpret the sensitivity of Zircaloy grain boundaries to iodine.

The chemical effects related to iodine would therefore seem to play a dominant role. However, a sample immersed in 1% iodated methanol is damaged after several days whereas slow tensile stresses applied in iodated methanol at concentrations a thousand times weaker lead to crack initiation after just a few hours. Consequently, mechanical stress clearly plays a powerful role in the crack initiation process.

5.2. Role of plasticity

No stress corrosion crack initiation was observed after slow tensile tests performed in an inert atmosphere. Stress alone is not therefore sufficient to damage the surface. Now the absence of any surface damage on a test specimen subject to an applied stress approaching the elastic limit in iodated methanol would seem to indicate that it is the plastic strain of the stressed material more than the applied stress which plays the dominant role.

This role appears indirectly in certain studies. For example, Haddad [42], using Laüe's determination of the crystallographic orientation of very coarse grains, showed that there is no correlation between time to failure and resolved stress on the base plane, even though the cracks are observed in grains with the most favourable orientation for failure on the base plane. This could be attributable to the initiation stage and could prove that stress level is not the governing factor in this stage. Similarly, Sejnoha and Wood [43] showed that scratches deliberately made in the surface of a Zircaloy sample subsequently subjected to iodine-induced SCC, do not induce crack initiation: it may thus be concluded that crack initiation is not governed by stress concentrations.

Moreover, it has been shown that the crack density increases with local strain. This result is in agreement with previous observations [18,19]. In view of the low work-hardening of zirconium, two possibilities may be considered to explain this local strain effect: the existence of high microscopic stresses (this possibility is discussed in the second part of this paper) or mechanical depassivation linked to the local failure of the oxide film by the emergence of slip bands.

For SCC models of the corrosion–plasticity interaction type [29], cracking always starts by a mechanical depassivation mechanism linked to the surface emergence of slip bands. This is an all or nothing mechanism for which the existence of slip bands is associated with total failure of the film which is assumed to be not ductile. Indeed, a correlation has even been established [44] between the stacking fault energy (and thus the planar slip tendency) and the susceptibility to SCC of austenitic stainless steels in chloride-rich atmospheres. Unfortunately, to the authors' knowledge, no data are available on the mechanical properties of passive films. Therefore, in cases of SCC for which an anodic dissolution model is applicable, the parameter ϵ_f is a general value that cannot be determined experimentally.

In the case of Zircaloy, a strain of 0.4% could be sufficient to break the oxide [19] and it may therefore be concluded that this mechanical depassivation mechanism plays a major role in the slow tensile tests performed.

However, mechanical depassivation by slip bands should, in theory, affect the bulk of the grain just as much as the grain boundary and so this cannot explain the essentially intergranular nature of the crack initiation process observed. Obviously it would be possible to imagine a higher level of mechanical depassivation at the grain boundaries. Indeed, it has been found that the areas located close to the grain boundaries are often subject to intense plastification: activation of additional slip near the boundaries, and even perhaps intergranular slip in certain cases. However, this would not seem to give a sufficient reason to explain the observations. Only a slight predominance of intergranular crack initiation over transgranular initiation would result in such an effect, and this is not the case.

6. Conclusions

In order to study crack initiation under iodine-induced SCC conditions in Zircaloy-4, slow tensile tests were conducted in an inert atmosphere and in a corrosive atmosphere (iodine vapour at 350°C and iodated methanol at 20°C) on plane test specimens of zirconium and Zircaloy-4. Detailed examination of the outside surface of these samples revealed that:

- no crack initiation could be detected following the tests in an inert atmosphere; in addition, large differences in strain from one grain to another and even inside the grains were noted; considerable localised slip in the vicinity of certain grain boundaries was apparent, even at 350°C;
- the chemical effects linked to iodine and the mechanical effects linked to applied stresses and subsequent strain, cannot be perceived separately. The stress corrosion initiation mechanism must therefore be analysed as a corrosion–strain interaction.

The crack initiation scheme would be as follows: local mechanical failures of the passive film on the Zircaloy surface take place during the slow tensile tests conducted. By adsorbing on the surface of the material, iodine is liable to change the film equilibrium conditions and destabilise it, thereby compounding the mechanical effects of the applied stress. In addition, the iodine may hinder film reconstruction since its adsorption at the bare metal surface would be competing with that of oxygen. This could, in particular, lead to the formation of a non-protective film and thus promote locally serious oxidation in an iodine vapour atmosphere at 350°C.

An intergranular corrosion process, assisted by the stress, plays a major part in the crack initiation mechanism. The macroscopic stress would promote the preferential opening of grain boundaries with planes perpendicular to the applied stress direction. In iodated methanol, because of the small quantity of oxygen available for reconstructing the surface film of the ma-

terial, this intergranular decohesion process would thus be facilitated.

The analysis of the possible role of plasticity was focused on the extent of local strain, the effect of which would appear to be related to mechanical depassivation. However, the essentially intergranular nature of crack initiation still requires further explanation. The intense plastification of the areas close to the grain boundaries could play a role, as could the greater brittleness of the passive film near the boundaries. These reasons would not seem to be sufficient; in the second part of this study the role of plasticity will be examined from the standpoint of local microscopic stresses liable to arise within the polycrystal.

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