Cracking Behavior In Inconel Alloy 690: Role Of The Environment In High Temperature H_2-Supersaturated Steam

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ABSTRACT Nickel base alloys 600 and 690 have found widespread applications in nuclear reactor steam generators. In particular, alloy 690 with a major element composition of typically Ni-30Cr-9Fe, has shown an apparent improvement in performance when compared with alloy 600 in both primary water and caustic environments. Nevertheless, alloy 690 can also be susceptible of undergoing hydrogen induced stress corrosion cracking (SCC). However, the role of the microstructural state is not well defined, such as the effect of the presence or absence of carbide precipitation along grain boundaries on the overall susceptibility. In this work, self-loaded linear elastic fracture mechanics M-WOL specimens made of alloy 690 were tested in both, the solution annealed condition (minimal grain boundary carbide precipitation), and after a grain boundary carbide precipitation treatment. Tests were carried out at 320-400^{o}C in an instrumented autoclave used to "in-situ" monitor crack growth rates. The environment was simulated by the generation of high-pressure supersaturated hydrogen steam. The tested M-WOL specimens were loaded under various applied K_I values (between 50-80 MPa $m^{1/2}$). This work discusses the role of the artificially imposed environment, as well as the kinetic and microstructural factors, which lead to crack propagation in alloy 690.

1 INTRODUCTION

Extensive work worldwide has been devoted to disclosing the mechanisms involved during the intergranular stress corrosion cracking (IGSCC) of pressurized water reactors (PWR) made of Inconel alloys [Env. Deg. of Mats. in Nucl. Power Sys-Water Reactors, 1988, Noel, *et al.*, 1996, Lenartova, *et al.*, 1996]. From these works, it is well known that Inconel alloy 600 is susceptible to SCC under hydrogen supersaturated steam at temperatures above 300^{o}C. Yet, the mechanistic aspects involved in the SCC of these alloys are far from being resolved [Shen and Shewmon, 1990, Foct *et al.*, 1996, Newman and Saito, 1992, and Bond *et al.*, 1988]. In general, it has been found that heat treating can lead to Cr depletion of the grain boundaries in precipitation hardened Ni-base alloys as a result of grain boundary chromium carbide precipitation (condition known as sensitized in other alloy systems) [Lenartova, *et al.*, 1996]. This condition should be highly susceptible to SCC, in contrast with the experimental reports [Shen and Shewmon, 1990]. Yet, these alloys become increasingly susceptible in the milled annealed condition [Env. Deg. of Mats. in Nucl. Power Sys-Water Reactors, 1988, Shen and Shewmon, 1990].

Moreover, it has been found that crack propagation occurs preferentially along grain boundaries [Shen and Shewmon, 1990, Foct *et al.*, 1996, Newman and Saito, 1992, and Bond *et al.*, 1988]. In addition, grain boundary segregation which can reduce the cohesive strength of the grained structure is not able to account for the IGSCC susceptibility for the present amounts of segregated impurities [Lenartova, *et al.*, 1996]. The role of hydrogen is not clear either. It has been found that dissolved hydrogen in high temperature steam enhances the IGSCC susceptibility in Inconel alloys at 300-360^{o}C in pure water [Noel, *et al.*, 1996]. In particular, it has been found that as the dissolved hydrogen concentration is increased, the time for cracking in PWR's decreases dramatically [Noel, *et al.*, 1996]. Yet the mechanisms proposed are not able to account for all the experimental facts.

Alternatively, when alloy 690 has been employed to replace alloy 600, the SCC susceptibility is significantly reduced under the PWR environments [Ehrnesten *et al*., 1996]. Apparently, increasing the Cr content from 15 % (alloy 600) to 30% (alloy 690) leads to improved cracking resistance. Although, there is not a clear explanation for this behavior, it seems that the alloy re-pasivation kinetics is enhanced at increasing Cr contents [Ehrnesten *et al*., 1996]. Electrochemical studies [Lenartova, *et al*., 1996] on the effect of hydrogen on the SCC susceptibility of alloys 600 and 690 indicate that the IGSCC is cathodic in nature as this effect is drastically enhanced under highly reducing conditions. Moreover, there is no clear evidence for hydrogen having a detrimental effect on the passive film properties of these alloys.

In addition, the activation energies associated with IGSCC in Inconel alloys have been reported to be of the order of 74-138 kJ/mol [Shen and Shewmon, 1990], which suggest Ni grain boundary self-diffusion as the rate limiting mechanism. Moreover, the reported activation energies seem to be inversely related to the applied stress intensity factor K_I in compact specimens [Shen and Shewmon, 1990]. Although, the IGSCC susceptibility of Inconel alloys has been extensively investigated, some of the relevant mechanistic aspects are still not clear. In particular, the role of hydrogen in either promoting localized plasticity, grain boundary decohesion, or the development of methane bubbles needs to be fully resolved. Accordingly, this work is an attempt to further investigate the active mechanisms involved during the IGSCC of an Inconel alloy 690.

2 EXPERIMENTAL METHODS

In order to investigate the kinetic aspects of IGSCC of Inconel alloy 690, the potential drop technique was employed. The method is based on using fracture mechanics compact M-WOL specimens coupled with the potential drop technique for "in situ" monitoring of crack propagation rates under fixed temperature and hydrogen supersaturated steam conditions. Figure 1 shows schematically the various components involved in crack growth monitoring using the potential drop technique. In this work, the Inconel alloy 690 investigated was in the as-received condition. Self-loaded LEFM specimens were machined from this alloy using the modified version of the wedge-opening-loading (M-WOL) developed by Novak and Rolfe [Shen and Shewmon, 1990]. These specimens can be self-stressed by the use of a bolt and a loading tup and they are shown schematically in Figure 2. In particular, the back-face-strain-technique [Shen and Shewmon, 1990] was used in measuring the applied stress intensity $K_{I.}$ The M-WOL specimens were fatigue pre-cracked following ASTM standard E-399.

Crack propagation tests were conducted in a high temperature static autoclave system were loaded at a fixed applied K_I of 60 MPa $m^{½}$ and then exposed to hydrogen supersaturated steam at various temperatures (300-400^{o}C). This environment is generated by initially placing 36 g water and 0.1 MPa hydrogen (25^{o}C). The autoclave has been instrumented (see Fig. 1) for in-situ monitoring crack growth rates using a data acquisition card, a personal computer, and the Klintworth analysis [Shen and Shewmon, 1990] for converting potentials to crack lengths. From these experimental conditions, it was possible to estimate the apparent activation energy for crack growth using Arrhenius plots of (da/dt) versus 1/T, where a is crack length, t is time and T is temperature.

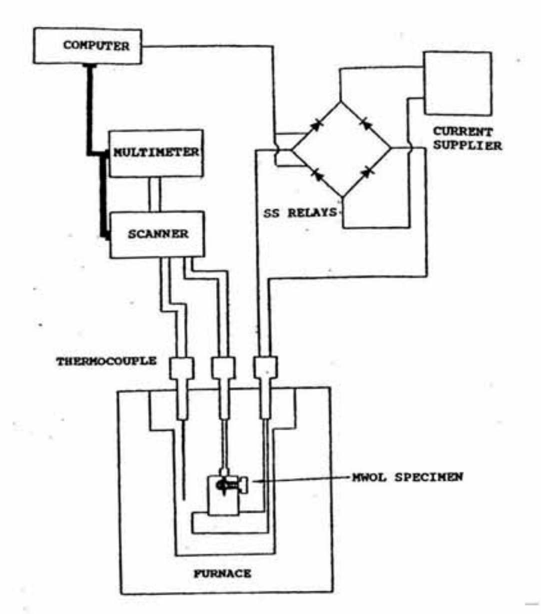


Figure 1. Schematic drawing of the testing apparatus used for crack growth rate measurement

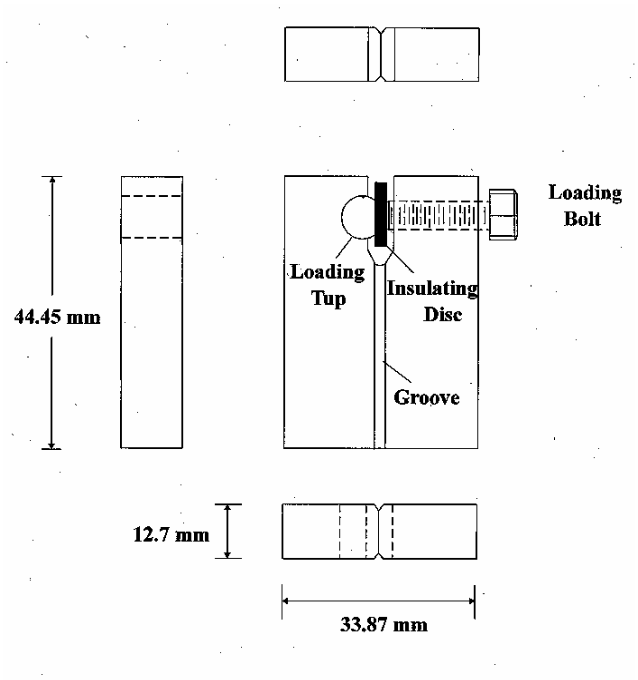


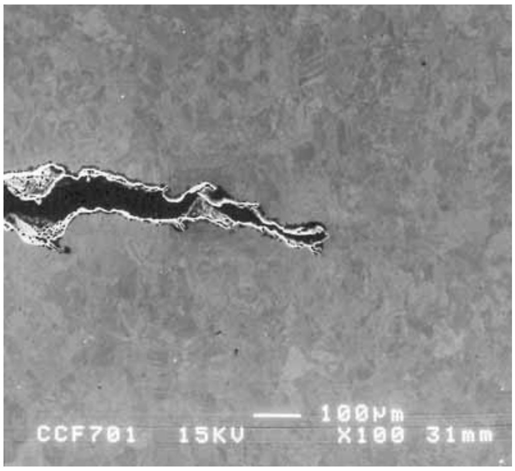
Figure 2. Schematic representation of the modified WOL specimen load assembly

The effect of applied K_I on the rate of crack growth was also estimated in the as-received alloy by exposing the M-WOL specimens to the SCC environment. These specimens were previously loaded at applied K_I values in the range of 29-90 MPa $m^{½}$and then exposed to hydrogen supersaturated steam at 370^{o}C. The as-received microstructure and type of carbides was evaluated by optical and scanning (SEM), electron microscopy. Also, crack paths and crack lengths, were characterized by these means.

3 RESULTS AND DISCUSSION

In the as-received Inconel alloy 690, the exhibited microstructure consisted of stacking faults and fine carbides, both within and along grain boundaries (Fig. 3a). Also, the path followed by these specimens was predominantly intergranular with some branching as shown in Figs 3a-b.

(a)



(b)

Figure 3. Crack paths exhibited in Inconel 690. (a, b) Notice the presence of grain boundary carbides, as well as significant stacking faults within the bulk, including some degree of crack branching.

Exposure of M-WOL specimens to hydrogen supersaturated steam enabled the determination of an apparent activation energy for crack growth (da/dt) in specimens loaded at 60 MPa $m^{1/2}$. The experimentally determined activation energy was of the order of 120 kJ/mol as shown in Fig. 4. which is in good agreement with the activation energy reported for grain boundary self-diffusion of Ni which is 115 kJ/mol [Shen and Shewmon, 1990]. The effect of the applied K_I on (da/dt) was also evaluated as shown in Fig. 5. Notice from this log-log graph a linear trend for crack growth with the applied K_I suggesting that there is a stable stage II for crack growth. Accordingly, crack growth can be described by an empirical expression of the type $da/dt = AK_I^n$ where n = 1. This in turn indicates that the mode of crack growth is linear with $K_{I.}$ However, there was significant branching in the specimens exposed to these environments (see Fig 6). Accordingly, it is not possible to disclose the mechanisms involved during crack propagation. Since crack branching becomes dominant, there is no simple meaning to the exhibited crack growth. Moreover, the nature of crack path seems to be of mixed mode with crack with intergranular and transgranular crack segments.

In addition, due to the cathodic nature of SCC crack propagation, this work will emphasize the role of hydrogen. From the work of Shewmon and co-workers [Shen and Shewmon, 1990]. alloy passivation can be described by

$$2/3Cr + H_2O = 1/3\ Cr_2O_3 + H_2 \qquad (1)$$

As a result of this reaction, it is likely to release hydrogen at the crack tip with extremely high fugacities. Increasing the Cr levels from 15 to 30 % will not diminish this effect. Enough hydrogen release will be available in the crack tip regions as fresh metal is exposed to H_2O.

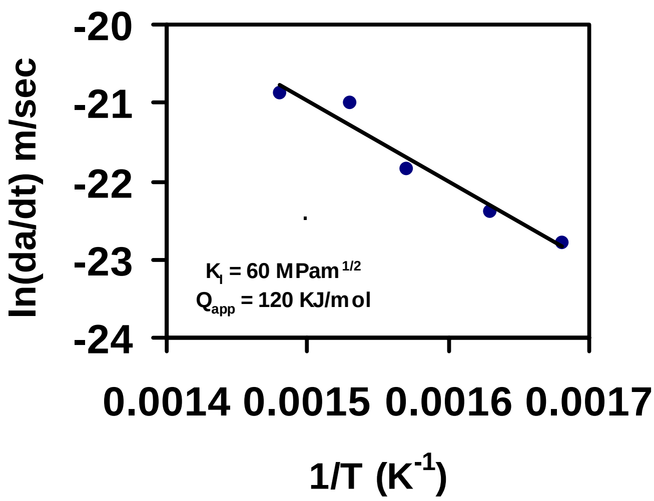


Figure 4. Arrhenius plot of ln(da/dt) versus 1/T for as-received alloy 690 M-WOL specimens exposed to hydrogen supersaturated steam under an applied K_I of 60 MPa $m^{1/2}$.

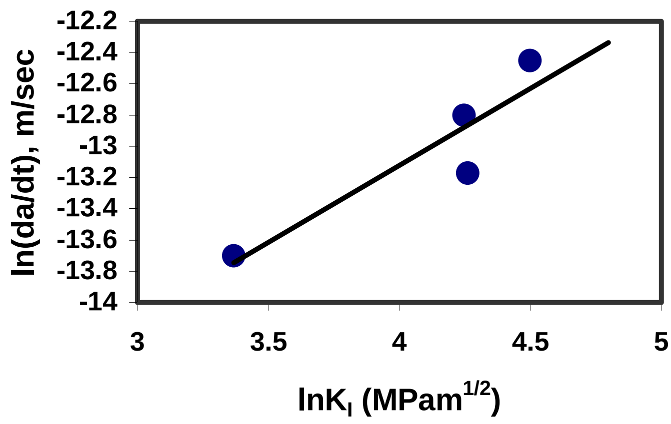
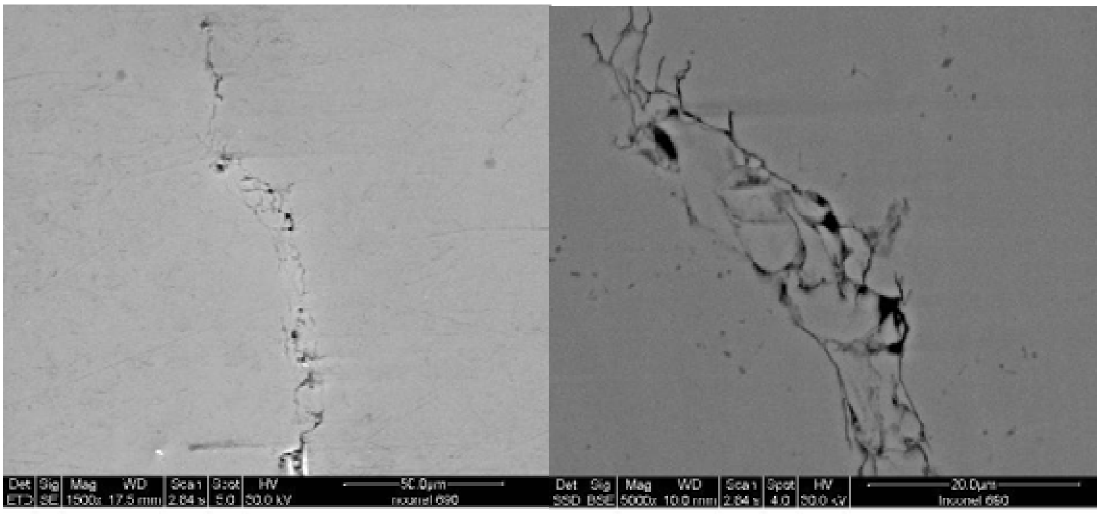


Figure 5. ln(da/dt) versus applied K_I for as-received alloy 690 M-WOL specimens exposed to hydrogen supersaturated steam at 370°C.

Evidence for this effect has been experimentally shown by Ehrnsten and co-workers [Ehrnesten *et al.*, 1996]. In their work, they found that when excess hydrogen was removed in an Inconel alloy exposed to hydrogen overpressure, the electric resistance of the Inconel surface as well as the potential drop signal, both increased significantly, indicating that the alloy was able to re-passivate according to reaction (1). Hence, high hydrogen fugacities product of reaction 1 developed at the tip of the crack which in turn promoted IGSCC. In the 300-400^{o}C range, hydrogen preferentially diffuses along the grain boundaries where it can react with segregated carbon to locally produce methane bubbles as described by Shewmon and co-workers [Shen and Shewmon, 1990]. The development of methane bubbles in turn is rate limited by the accommodation of the Ni-matrix to make room for the growing bubbles. In the present work, the experimentally determined activation energy of 120 kJ/mol indicates that Ni atom accommodation occurs preferentially by grain boundary self-diffusion. Since a fine distribution of carbides was found along grain boundaries as shown in Fig. 3a, it is expected that segregated carbon will be reduced to levels where methane formation might be minimal. Yet, alternative hydrogen effects might be active such as those suggested by Saario and co-workers [Saario and Aaltonen, 1995] in their model on the selective dissolution vacancy creep, or through hydrogen induced grain boundary plasticity, both of which can account for IGSCC.



(a) (b)

Figure 6. SEM backscattering micrographs showing the crack path in Inconel alloy 690. (a) crack bifurcation into two main cracks and crack interweaving and (b) detail of crack branching.

Finally, the rate of crack propagation dependence with the applied K_I indicates that stage II crack propagation follows an apparent linear trend with the applied stress intensity factor. However, when branching occurs, crack propagation should be independent of the applied K_I and crack length during stage II [Shen and Shewmon, 1990]. Since the degree of branching is minimal, under the SCC conditions employed, crack growth might exhibit a linear trend with the applied K_I to account for the experimental outcome, but further analysis is needed to resolve this issue.

4 SUMMARY

M-WOL specimens of alloy 690 were exposed at 300-400^oC in deaerated hydrogen supersaturated steam under an applied stress intensity factor (K_I) of 60 MPa $m^{1/2}$. It was found that the alloy exhibited a mixture of transgranular and intergranular stress corrosion cracking in the as received condition. An activation energy of 120 kJ/mol was found which is close to the one reported for grain boundary self-diffusion of nickel indicating that intergranular accommodation of the Ni-matrix was dominant during SCC. The corrosive environment was predominantly cathodic in nature. Hence, high hydrogen fugacities product of reaction 1 are expected to be developed at the tip of the crack which in turn promote stress corrosion cracking.

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