

A Mechanism for Hydrogen Induced IGSCC in Inconel 600

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ABSTRACT

Intergranular stress corrosion cracking (IGSCC) of INCONEL 600 in high temperature deaerated water has been termed 'hydrogen induced IGSCC'. It is suggested here that these cracks are initiated by the nucleation of a high density of methane bubbles on the grain boundaries under the combined action of the applied stress, and high pressure methane formed from carbon in solution reacting with hydrogen injected by corrosion. The bubbles then grow together to give local failure by grain boundary diffusion. The thermodynamics and kinetics of this process are examined and shown to be in quantitative agreement with several experimental observations. The mechanism involves no dissolution of the metal, the role of corrosion being the injection of hydrogen at a high fugacity.

KEYWORDS

INCONEL 600, Stress Corrosion, Cracking, Hydrogen

Several years ago Coriou et al. showed that INCONEL 600 would exhibit intergranular stress corrosion cracking (IGSCC) in deaerated water at 300-350C [1]. These results were initially questioned since there had been no history of service failures with the alloy in such an environment. However, since then there have been numerous reports of IGSCC originating in the pure, oxygen free water on the primary side of the steam generators of pressurized water reactors [2]. It is now well known that depending on the environment INCONEL 600 can exhibit two quite different mechanisms of IGSCC which depend differently on the distribution of chromium carbides in the alloy. The precipitation of carbides at grain boundaries (sensitization) enhances IGSCC of this alloy in acid solutions at room temperature, as well as in aerated water at high temperatures, but the same alloy in the solution annealed condition is resistant to IGSCC in these environments [3]. In contrast, the reverse is true for hydrogen induced IGSCC, namely, sensitization makes INCONEL 600 more resistant to IGSCC in deaerated water, or steam, at high temperatures, while solution annealing increases the rate of attack [4].

It is generally agreed that the cracking of sensitized INCONEL 600 in aerated water occurs by the anodic dissolution of the chromium depleted regions around the grain boundary carbides. But, there is no general agreement on how the cracking develops in the solution annealed metal in deaerated water under conditions where electrochemical metal dissolution is impossible (cathodic conditions), and the chromium concentration is uniform across the boundary.

An important element in the argument is the accelerating effect of hydrogen on the rate of IGSCC in solution annealed INCONEL. Results obtained by Smialowska and others have shown that:

- 1) The cracking occurs in water under conditions (electrochemical potentials) where hydrogen is evolved [5].
- 2) Saturating the water with an overpressure of one to a few atmospheres hydrogen accelerates the cracking, but the rate goes through a maximum at about 5 atm and is retarded by higher hydrogen concentrations [6].
- 3) Cracking occurs at comparable rates in deaerated water or steam.
- 4) Cracking does not occur at these temperatures (300-400C) in pure dry hydrogen, at least up to 5000 psi.
- 5) The accelerating effect of hydrogen is strongly enhanced by stresses and strains in the alloy [4,7].

KINETICS

In the model developed below it is argued that the hydrogen injected into the metal by corrosion can react with the carbon in solution to form high pressure methane which aids the nucleation of bubbles along the grain boundaries of INCONEL 600. This nucleation generates such a high density of bubbles that the bubbles can grow together by grain boundary diffusion in a time sufficient to give the observed crack growth rates of about 5 $\mu\text{m/hr}$. This growing together of holes by grain boundary diffusion is similar to that found in high temperature creep failure, but occurs more rapidly even at a low temperature because the distance between holes is an order of magnitude smaller than that found in the case of high temperature creep. The two central questions of kinetics for this model are thus:

- Can the stress across the boundary and the methane pressure combine to give conditions where rapid homogeneous nucleation of bubbles on the grain boundaries can occur?
- What bubble spacing is needed for boundary diffusion limited growth at the observed rates, and is it a credible spacing? Can it be observed?

Nucleation

The equation for the nucleation of voids on grain boundaries in solids is of the form

$$N = AD_b \exp(-G^*/kT) \quad (1)$$

where N is the number of nuclei formed per cm^2/s , A is a constant, and D_b is the boundary diffusion coefficient which enters because vacancies must diffuse along the boundary to make up the clusters which form voids [8]. A detailed consideration of the equations involved shows that N is large when $(G^*/kT) < 100$. For the nucleation of bubbles with an internal pressure P on a grain boundary with a normal stress σ_n , the equation for G^* becomes [9]

$$G^* = (P + \sigma_n)V^* - (P + \sigma_n)[4\pi r^3 f(\theta)/3] = 16\pi\gamma^3 f(\theta)/3(P + \sigma_n)^2 \quad (2)$$

V^* is the volume of a nucleus of critical radius $r^* = 2\gamma/(P + \sigma_n)$, where γ is the surface energy of the solid-gas interface. The parameter $f(\theta)$ is introduced to allow for the decrease in volume of the critical nucleus if the surfaces between the matrix and heterogeneities such as grain boundaries are eliminated by the nucleation. The contact angle of the bubble on the heterogeneity is θ . Because of the high density of bubbles necessary for this model, there are no second phase particles in the annealed alloy that can generate the high density needed. Thus the only heterogeneity of importance is the grain boundary. Grain boundary energies are about half to one third of a clean surface. This gives $f(\theta)$ of about 0.9.

In considering this model we assume that the equilibrium methane pressure can develop in embryonic bubbles during the time they develop into viable nuclei in the solid. It is known that the kinetics of methane formation is fast enough to develop the equilibrium methane pressure in voids in steel at temperatures of 300C and above [10,11]. Also, nickel is a better catalyst for the formation of methane than is iron. The uncertainty is in whether the methane can form on the time scale and within the dimensions of the embryonic bubbles of interest here. We postulate such equilibrium exists.

The equilibrium methane pressure is determined by the activity of carbon and the fugacity of hydrogen through the equilibrium constant. The activity of carbon is the ratio of the amount of carbon in solution in the supersaturated alloy to the concentration that would dissolve in the alloy in equilibrium with graphite, with the formation of no additional chromium carbides. The solubility of carbon in INCONEL 600 at the solution annealing temperature of say 1000C is about 0.03% [12]. This carbon is all kept in solution by a quench (though quenches from higher temperatures, with more carbon in solution, will not keep all the carbon in solution [13]). 0.03% exceeds the solubility of C in Ni at 350C by almost an order of magnitude [14]. However, the Cr in the INCONEL reduces the activity of carbon relative to that in Ni by about a factor of 100 [15]. For the purposes of our estimate, the activity of carbon in the solution annealed INCONEL 600 is estimated to be 0.1 that of graphite. If the alloy were cooled more slowly from 1000C, chromium carbides would form on the grain boundary and the concentration of carbon in the lattice at the boundary would be lowered by a factor of 30 to 60 [14]. The carbon activity is thus lowered substantially by the sensitization.

The hydrogen fugacity is harder to estimate. The corrosion of an alloy like INCONEL 600 can give extremely high fugacities of hydrogen [16]. We have tried to produce cracking in solution annealed reverse U-bend samples of INCONEL 600 with a dry hydrogen atmosphere at a pressure of 29 MPa at 400C, but no cracks formed. However, tests on the same sample (or others) in steam containing one atmosphere of hydrogen produced cracking in a few days at this temperature. It also injects concentrations of hydrogen well above that which would be in equilibrium with 29 MPa of hydrogen [7]. We will assume that the effective hydrogen pressure beneath the corroding surface is four times this or a fugacity of 120 MPa. For these conditions the correlation suggested by Odette and Vagarali [17] gives an equilibrium methane pressure of about 1100 MPa. Due to the non-ideality of methane, its pressure changes slowly with fugacity under these conditions. Thus doubling the hydrogen fugacity of 240 MPa would increase P for methane by only 10%.

The residual stress acting normal to the grain boundary would be about equal to the yield stress, and is taken to be 500 MPa. The surface tension for clean nickel is about 1.6J/m^2 , but hydrogen has a significant heat of

adsorption [18] (23 kcal/mol) which would reduce the surface tension appreciably. If we take γ to be 0.8J/m^2 , the critical radius, r^* , is 1nm . This a factor of 2 larger than the radius at which $(G^*/kT)=100$ for this value of $(P+\sigma_n)$. Given the uncertainty in the value of γ and other factors, it is quite credible that on certain boundaries the stress in the lattice and the internal methane pressure is sufficient to nucleate bubbles homogeneously along the grain boundary, that is without the aid of precipitate particles.

If sensitization occurs, the carbon activity and the equilibrium methane pressure decrease by an order of magnitude. The equilibrium methane pressure is much less than σ_n , the term $(P+\sigma_n)$ decreases by only 3, G^* drops by 9, and the nucleation rate by $\exp(9)$. This is enough to retard the nucleation, but not enough to stop it. Experimentally it is observed that sensitization retards IGSCC, but does not stop it. Plastic strain might affect the nucleation by the formation of dislocation pileups at grain boundaries creating embryonic cracks which would aid nucleation.

Growth

Figure 1 shows the unetched surface of a sample in which IGSCC developed at 380C in steam. Note the family of small cracks all of which run along grain boundaries. Most are also roughly parallel and in a plane running normal to the residual stress in the surface. One crack has grown larger, and thus relieved the stress driving the other cracks. It is the rate of growth of this lead crack that is of interest to us here. Fig. 2 shows a schematic of our model for what is happening beneath the surface of the metal with the lead crack. It shows the bubbles developing beneath the interface between metal and environment (steam or water). Corrosion where the wet environment meets the root of the growing crack will develop a high local concentration of hydrogen in the lattice in this narrow region. Hydrogen will diffuse from this line into the rest of the sample which has a much lower hydrogen concentration. Thus bubble nucleation will only occur in the region near the crack tip where the hydrogen concentration is highest. Before bubbles can nucleate deeper in the sample and the crack advance farther, the bubbles must grow together to link up.

One way to check the model against observations is to determine the bubble spacing necessary for bubbles on a grain boundary to linkup in the time the crack needs to advance one grain diameter. The time for an array of grain boundary bubbles of spacing $2b$ to grow by grain boundary diffusion to cover half the grain boundary area is given by the equation [9,19]

$$t_g = \frac{0.01 kT(2b)^3}{\delta D_b \Omega (P + \sigma_n)} \quad (3)$$

The experimental value for δD_b in pure Ni is $2.8 \times 10^{-15} \text{m}^3/\text{s} \exp(-13,800/T)$ [20]. At 350C the observed growth rate is $10 \mu\text{m/h}$ ($3 \times 10^{-6} \text{mm/s}$) [5]. Fig. 2 shows the shadowed replica of a region near a crack in a sample the underwent IGSCC. The fine white fingers arise from a high density of discrete pores in the grain boundaries. These pores nucleate as discrete small bubbles farthest from the main crack (which is just visible at the top of the figure), and then grow into a more dense, unresolvable, set of bubbles closer to the surface.

Our model thus postulates that fresh bubbles nucleate on grain boundaries at a distance, d roughly $20\text{-}40 \mu\text{m}$, below the interface between the environment and the metal, and that these must grow together in a time t_g before the

aggressive environment can pass that point and initiate bubble growth yet more deeply. If $20\text{-}40 \mu\text{m}$ is the depth of the region that forms bubbles in front of the crack, the bubbles would have to link up in 2 to 4 hours to grow at a velocity $v_{\text{crk}} = d/t_g = 10 \mu\text{m/h}$. The value of $(P+\sigma_n)$ in Eq. 3 will decrease with time. The stress will remain constant but the formation of methane in the growing bubbles will quickly drain the surrounding lattice of its carbon, and rapidly reduce the equilibrium methane pressure in the bubbles to well below that which initially aided the nucleation. Taking $P=500 \text{MPa}$ (half its maximum value) gives $P+\sigma_n = 1000 \text{MPa}$, and a bubble spacing $2b = .32$ to $.41 \mu\text{m}$. Or, in the limit of $P=0$, $2b = .26$ to $.33 \mu\text{m}$. The spacing in Fig.2 where the pores are clearly separated is about $.2 \mu\text{m}$. This spacing is almost a factor of 10 finer than other examples of fracture by the diffusion limited growth of grain boundary pores, such as high temperature creep fracture, or the hydrogen attack of steels. However, it is much coarser than the density that could be generated by homogeneous nucleation; no doubt there is some competition between neighboring bubbles which reduces the density from that generated by nucleation to the stable size which grows to give IGSCC. The largest uncertainty here is in the proper value of δD_b to use. In going from pure nickel to INCONEL 600, alloying elements and adsorbed solutes could easily change δD_b by an order of magnitude, probably shifting it to lower values and requiring still smaller spacing to give the observed growth velocity.

DISCUSSION

The model developed above makes several predictions which compare well with experimental observations:

- 1) It explains how cracking can occur in the absence of electrochemical dissolution and why it is fastest when the alloy has the maximum amount of carbon in solution in the matrix. Thus the attack rate is reduced when the alloy is slowly cooled, when the carbon content is quite low, or when the carbon content is so high that the usual mill anneal will not avoid the precipitation of carbides on cooling [13].
- 2) It is credible in that the forces available in the system can give the required nucleation rate. Also, it allows one to calculate a crack growth rate which agrees with observed rate.
- 3) The predicted activation energy, equal to that for grain boundary diffusion of nickel in the INCONEL grain boundary, agrees with the reported activation energies for IGSCC under these conditions. That is, the activation energy for grain boundary self diffusion in nickel is 115kJ/mol while the reported values are 138kJ/mol (Bandy and Van Rooyen [4]) and 74kJ/mol (Totsuka and Smialowska [21]).
- 4) It explains the sensitivity to cold work and residual stresses, especially in material where the carbon activity has been reduced by an anneal which precipitates carbides.

An area where the model makes a clear prediction, but there is inadequate data to check it is the stress dependence of the crack growth rate. If one defines a stress exponent as 'n' in the equation $v_{\text{crk}} = A\sigma^n$, our model predicts $n=1$ if the internal methane pressure is zero during most of the bubble growth, and $n<1$ if P is comparable to σ . We know of no good data on the stress dependence of v_{crk} for hydrogen induced IGSCC, so no check on this is possible. However, the value of $n=1$ is clearly different from the stress dependence reported for IGSCC under anodic conditions. Here a stress exponent of about 5 is reported, and rationalized with a model in which v_{crk} is determined by the rate of metal creep around the advancing crack which in

turn leads to the fracture of the protective oxide layer at the crack tip.[22] The stress dependence of v_{crk} provides one way to distinguish a pore growth model from a localized dissolution model.

The effect of cold work on the rate of IGSCC is well documented. For example Brand and van Rooyen show that v_{crk} is a factor of 4 greater in cold work INCONEL than in annealed material. However, the activation energy for the worked and annealed material is the same. Cold work would be expected to increase the ease of nucleating grain boundary voids. This has been clearly shown in studies of the creep ductility of nickel base alloys cold worked at room temperature before high temperature creep [23,24]. Also, cold work of pure nickel before fatigue at 300-400C substantially increases the density of grain boundary voids and decreases the time to fracture [25]. If the bubble density increased by a factor of 3 in INCONEL 600 tested in the range of 300 to 350C, and the bubble growth mechanism remained the same, our model would fit the observations.

Finally, if pore growth and linkup leads to IGSCC, why doesn't the fracture surface observed in the SEM look like that found on fracture surfaces formed by high temperature creep or hydrogen attack which also occur by the diffusion controlled growth of pores, though with a pore spacing that is 10 times greater? I don't know, but suspect it has to do with the resolution of the SEM which is very good at the 2000x used to examine creep fractures, but is poor at the 20,000x required to show the same type of structure on the finer scale postulated here. The surface structure may also be influenced by a change in the micromechanism of fracture on the finer scale. That is, can shear lips form during the last stage of fracture to make dimples around the pores when the scale is a factor of 10 smaller? We are doing some work with a scanning-transmission electron microscope (STEM) which has much better resolution at the 20,000x level and hope to resolve this issue.

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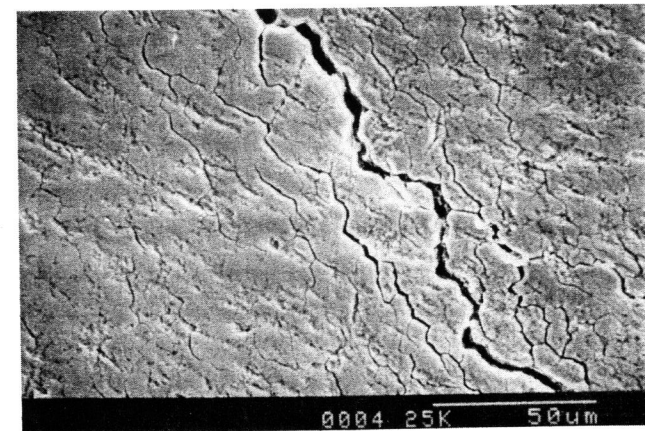


FIG. 1. Unpolished, unetched surface of a reverse U-bend sample of INCONEL 600 after formation of IGSCC in saturated steam, plus 1 atm (STP) of hydrogen, at 380C for 400 hr.

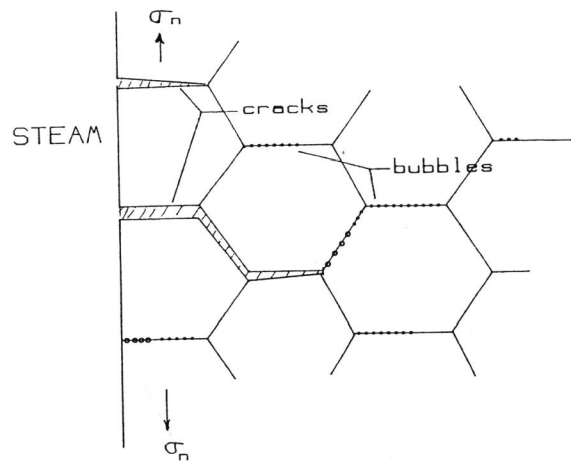


FIG. 2. Schematic section through a sample undergoing IGSCC by the nucleation and growth of bubbles into cracks. (The size and spacing of the bubbles is greatly exaggerated relative to the grain diameter to make the bubbles visible.) The corrosive environment (steam or water) can only penetrate to the end of the cracks. The cracking proceeds beneath the surface by the nucleation, growth and linkup of bubbles. The forces driving the bubble growth are the normal stress σ_n , and the internal methane pressure.

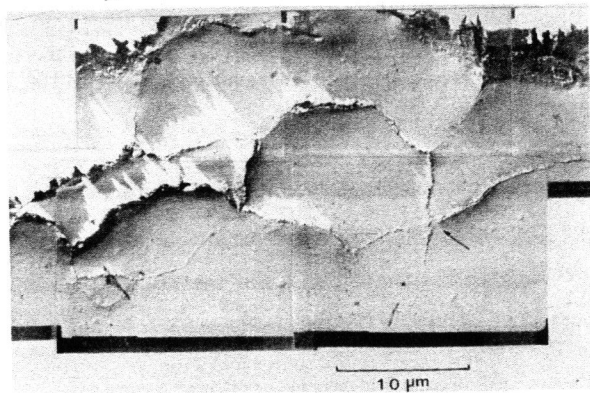


FIG. 3. Pt-Ir shadowed replica of region near IGSCC crack of sample shown in Fig. 1 showing high density of pores in boundaries near crack. There were no such bubbles in boundaries farther from the crack. Note the higher density of bubbles on the boundaries parallel to the crack (with higher tensile stresses across them) than those normal to the crack. The spacing of the discrete bubbles farthest from the main crack is about $0.2\mu\text{m}$.