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STRESS-CORROSION CRACKING OF INCONEL ALLOY 600 IN HIGH-TEMPERATURE WATER - An Update

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ABSTRACT

Inconel 600 has been tested in high temperature aqueous media (without oxygen) in several tests. Data are presented to relate failure times to periods of crack initiation and propagation. Quantitative relationships have been developed from tests in which variations were made in temperature, applied load, strain rate, water chemistry and the condition of the test alloy.

INTRODUCTION

Inconel* alloy 600 tubes in pressurized water reactor (PWR) steam generators form a pressure boundary between radioactive primary water and secondary water - the latter being converted to steam for generating electricity. Under operating conditions the performance of alloy 600 has been good, but with some occasional small leaks resulting from stress corrosion cracking (SCC), related to the presence of unusually high residual or operating stresses. There have also been a few minor leaks that were not positively identified as stress corrosion cracks because the tubes were merely plugged without removal for examination. The suspected high stresses can result from either the deformation of tubes during manufacture, or distortion during abnormal conditions such as denting. It is not yet certain what long-term effects are to be associated with lower stress levels that would be encountered during usual temperature cycles of a steam generator in service.

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*Trade name of the International Nickel Co.

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A primary to secondary leak causes contamination of the environment to some degree, as well as costly outages. The Nuclear Regulatory Commission (NRC) is involved in a licensing decision whenever leaks are reported and the utility would like to know how to adjust their repair schedule and tube plugging or sleeving progress. Both groups would, therefore, benefit from data that could be used for predicting or estimating failure times when abnormal conditions are encountered. A program is active at present at Brookhaven National Laboratory to examine the factors involved in the SCC of alloy 600 in high temperature deaerated water, with the objective of developing a model that will relate life expectancy of tubing to factors such as stress, strain, strain rate, environmental conditions, microstructure and cold work of the material. Such a model is intended to form the basis for determining a predicted life expectancy for an "unknown" by extrapolating one or two accelerated data points to operating conditions. This could then be used in various cases to assist in determining tube plugging or inspection criteria by using relationships involving SCC initiation and crack propagation rates.

The present experimental program addresses two specific conditions, i.e., 1) where deformation occurs but is no longer active, such as when denting is stopped and 2) where plastic deformation of the metal continues, as would occur during denting. Laboratory media consist of pure water as well as solutions to simulate environments that would apply in service; tubing from actual production is used in carrying out these tests. The environments include both normal and "off" chemistries for primary and secondary water.

The results reported here were obtained in several different tests. The main ones are 1) split tube "reverse" U-bends, 2) constant extension rate tests (CERT), and 3) constant load. The temperature range covered is 290-365°C. The data are intended to update work that was previously reported by Bulischeck and van Rooyen (1,2).

EXPERIMENTAL

Procedures are described in detail in two earlier papers (1,2) and are only repeated here in brief.

The susceptibility of alloy 600 to IGSCC is considered by many workers to be dependent on the microstructure produced during its processing history and its chemical composition. Theus and Domian, et al. demonstrated that materials containing low carbon concentrations crack more rapidly than those with higher levels (3,4). Out of 30 heats of material used in the BNL program, only the low carbon end was chosen for further work. Table 1 lists the chemical compositions and mechanical properties of the alloys used in this program as supplied by the producers. Heats are mill-annealed production-type steam generator tubing, except heat #6, which was used only in a few tests; this heat was received as cold worked and further heated in the laboratory.

Distilled demineralized water was used as starting liquid having a conductance of 0.5 μS. Additives were made as needed. Solutions were deoxygenated by successive pressure-vent cycles followed by steaming off 10% of the pressure vessel contents, to reach an oxygen concentration of 0 to

5 ppb. Primary water exposures were carried out in circulating systems with a flow rate of 0.38 L/h(0.1 gal/h). The solution chemistry was maintained at 10^{-4} M LiOH and 650 ppm of boron as boric acid with an H_2 overpressure of 0.1 MPa (15 psig). Oxygen removal in this system (or the one with H_2O + H_2 only), was achieved by repetitive pressure-vent cycles of the reservoir with H_2.

U-bend specimens were prepared from tubing that was split on its longitudinal axis and then bent with a modified tubing bender so that the inside surface of the tubing was in tension.

The incubation period required for crack initiation in relatively nonaggressive environments was found to be much longer than that necessary to produce substantial crack growth; therefore, since inspections were carried out at two-week intervals, the time at which cracks were just visible in a U-bend specimen was taken as the initiation time.

The CERT apparatus is a modified version of one originally designed at the General Electric Company.(5) A linear variable differential transformer (LVDT) was used to monitor the specimen extension and a load cell to measure the load. Both of these parameters were continuously recorded during the test. The extension rate range of this system is 10^{-4} to 10^{-9} sec^{-1}.

Tensile specimens were fabricated from tubing that was split along the longitudinal axis and tested in the curved, as received shape. Earlier tests (1,2) had been done with flattened tube tensile pieces. The faces corresponding to the inside and outside wall of the tubing were not machined or polished. In order to examine the effect of cold work, tests have been selected where the degree of cold work will be precisely controlled.

Constant load testing was done using tensile specimens cut from tubing in the as received condition; without flattening. The dead load was applied by means of a lever arm (ratio about 10:1) via a 10 mm pull rod that passed through a teflon seal into the autoclave. Four specimens per autoclave could be tested simultaneously in each autoclave. A dial gauge was used to measure the deflection at each lever arm during test, and a timer was de-activated on failure of a specimen. Solutions and stagnant or flowing conditions were used as described above.

RESULTS AND DISCUSSION

U-BENDS:

Cracking, when present, occurred on inside surfaces of the split U-bends which were exposed in tension. The earlier series of experiments had suggested a possibility that the carbon level of the alloy 600 influences the crack initiation/temperature relationship. Specifically, activation energy seemed to increase with increasing carbon content. These data were based on cracks observed in the temperature range 325°C to 365°C, with most of the data from the highest temperature levels. Since the temperature range is small, it was believed important to verify that this effect persists down to operating temperatures. There is also some scatter in stress corrosion data in general, and the present tests are no exception; therefore, a statistical analysis was deemed necessary and tests were started in the first half of 1981 using a larger number of replicate samples exposed in water at 290° and 315°C. These U-bends had been in test for 60 weeks at the previous inspection without any observed cracking; it should be noted that little or no cracking is expected during such a short exposure. Figure 1 repeats the earlier activation energy data points based on the U-bend tests, and Figure 2 shows the present earlier status of the U-bends being exposed. For the 0.02% C material, one test at 290°C and one at 315°C have now just exceeded, without SCC, the times at which SCC would have been predicted by extrapolation. The expected failure times based on a linear relationship are shown in Table 2. At least for 0.02%C, therefore, the activation energy may be greater than 36 Kcal/mole over the lower temperature range, which includes operating temperatures, although the ongoing tests are not yet out of this range at present. The other materials (.01, .03 and .05%C) have yet to reach points of intersection with the extrapolations of the high temperature portions of the curves. When sufficient data are available, we will use statistical methods (such as Weibull) to develop the final, quantitative model. The heats that were added at 290 and 315°C cover only the range of 0.01 to 0.03% C, while a few (8) of the original specimens with 0.01, 0.02, 0.03 and 0.05% C remain in the 290°C test. The latter 8 samples have reached 192 weeks without SCC. There were no cracks in the group of 36 U-bends stopped at 150 weeks, and, in retrospect, these may have been worth continuing even though they were duplicates of many heats, some of which were not expected to crack.

Constant Extension:

CERT data already reported showed a definite distinction between the initiation and propagation stages of SCC. Cracks did not initiate at the start of the test or the onset of plastic deformation, but took a finite time (after that) to develop; initiation times were, however, much shorter than in the U-bend exposure. Extrapolations to zero crack length were made to determine the onset of SCC in CERT at temperatures of 325°C, 345°C and 365°C, using specimens made from production tubing, flattened before cutting tensile specimens. In continuing this work, for the present, corrections were based on the old curves and used for calculating crack propagation rates in as-received, undeformed materials. This is being done while similar initiation corrections are being developed for as-received tubing. Cracking in the CERT was achieved readily in as-received material at strain rates in the vicinity of 2×10^{-7} sec^{-1}. As shown below in more detail, the activation energies for cold worked and non-cold worked alloy 600 were found to be identical, suggesting that the mechanism is the same in the two cases, although the crack growth velocities for the types of specimens were different.

Figures 3 and 4 show the straight line Arrhenius plots of CERT data obtained to date repeating the curve, published earlier, for comparative purposes. As can be seen, several more sets of data points are now available, and all of them provide parallel curves that correspond to an activation energy of 33 Kcal/mole. Some pertinent observations based on the CERT data are detailed briefly below.

The slopes of the lines remained consistent with an activation energy of 33 Kcal/mole regardless of the state of the material. At any given temperature crack growth variations were due to a change in the constant k of the Arrhenius equation:

$$\text{Rate} = k.\exp\left(-\frac{Q}{RT}\right)$$

Environmental conditions appeared to affect the quantitative aspects of cracking in CERT. Hydrogen (added to pure H_2O) increased the number of cracks as well as SCC growth rate of as-received material; H_3BO_3 (added to pure H_2O) did not show the same effect. Other combinations of the ingredients of primary and secondary water are in test now, and the initial point for primary water at 365°C appeared to be near the one for the $H_2O + H_2$ combination. Both environments are being examined further. For the completed data, it is believed feasible to test an "unknown" tube in one accelerated test to establish its initiation and propagation rates, and then calculate data for other temperatures from this determination. In other words, the test at a single high temperature fixes the curve for that tube.

Cold worked (flattened) specimens gave crack growth rates in simulated AVT and primary water consistent with rates observed in pure water. Tests with as-received material in these two media are expected to parallel the results mentioned. Specimens aged (furnace) at 365°C for several weeks before exposure in pure water (CERT) gave crack growth rates similar to fresh material, when tested as cold worked (flattened), and the lack of effect is apparent for non-cold worked tubes.

Crack growth velocities in our work are in the same ranges as were found in published work for tests is sodium hydroxide solutions at elevated temperatures. (See Figure 4). The effect of reducing strain rate on crack velocity was not very severe, but varying strain rates in the range 4×10^{-8} to 7×10^{-7} sec^{-1} were responsible for a reduction in crack velocities by about a factor of 2. Therefore, the lowering of the strain rate at lower temperatures, needed to allow time for SCC propagation, may give velocities that are on the low side unless corrected. This correction may equally be made by lowering the values obtained at higher rates. Most of the present tests were done at about 2×10^{-7} sec^{-1}, in order to keep the basis for our curves as constant as possible.

Extrapolation of data from cold worked samples shows initiation at approximately 12% strain at operating temperature, as shown in Figure 5. This number appears to be in good agreement with what has been observed in ovalized tubes when denting led to SCC in alloy 600 tubing. A comparison of SCC times based on the laboratory data (using susceptible tubing) with the field observations shows considerable promise that the laboratory data would be accurate when used to predict service performance. An example of an extrapolation is given as follows, but must not be taken yet as a final, accurate calculation because our basis is not sufficiently complete:

Laboratory tests for as-received material in pure water indicate a crack velocity at 300°C of about 5×10^{-8} mm sec^{-1}. In order to achieve observable cracking in the CERT, strain rates at these low temperatures appear to be of the order of 1 to 5×10^{-8}. Assuming that a strain rate of 2.5×10^{-8} is observed, we can use this to show that it will take about two months to reach roughly 12% strain at which time cracks will initiate. At this temperature (for tubing that has not been cold worked), the crack velocity will be approximately 5×10^{-8} mm sec^{-1} based on presently available data, so that it would take approximately four to six months for cracks to propagate 60% through wall. A series of more accurate calculations will be made within the next few months when more refined data are available, including simulated primary water. However, it is evident that reasonable predictions can already be made for the case of active deformation. It has to be emphasized that service conditions will affect the calculations, and that the accuracy will depend to a considerable degree on what is known about in-service strain rates, temperature, degree of deformation, and material susceptibility. No amount of laboratory studies such as we are doing can be substituted for this information.

Figure 6 shows a comparison of the stress-strain curve for heat #2 in the as-received, mill annealed condition, with another that had first been subjected to a heat treatment of 20 hours at 700°C. This latter treatment is equivalent to the latest commercial method used to induce chromium carbide precipitation, which is believed to provide resistance to SCC in deaerated high temperature water.(5) When tested earlier as flattened tensile specimens, the as-received material showed intergranular failure, whereas the material after 700°C treatment showed a ductile fracture with only extremely shallow intergranular penetration at one point on the surface. This work has not been extended to the as-received condition, since the latter has been found to be a less severe test than the one in which the benefits of the 700°C treatment for exposure to pure water at 365°C was demonstrated.

Constant Load:

For the case where denting or deformation is no longer active, it is necessary to obtain data that relate the time to failure to the stress present in the surface of the material, i.e., the load on that part of the tube. These stress patterns can consist of residual plus operational stress, and may be complex. In the present test series, a first attempt at relating load to SCC failure time was made by means of "as-received" tensile specimens under applied load. This will be compared with simulated dents in order to find out how the quantitative values compare for this type of failure in alloy 600. Figure 7 shows the curves for stress versus failure time on logarithmic scales, including results for as-received and cold worked material. In the equation $T_F = k.\sigma^b$, the slope of the two parallel log-log curves provides a value of $b = -4.0$, in the range that has been studied so far. This confirms the value for b for cold-worked specimens which was based on fewer data, and which is included in Figure 7. Figure 8 shows initial points of data obtained in simulated primary water at 365°C as well as for pure water with added H_2, where the slope agrees with the pure water plots. In caustic testing, Theus has also reported SCC in terms of applied stress, and this has shown cracking at stresses well below the yield point.(3)

In the cold worked material, (resulting from the flattening of the tube specimens during the preparation of the tensile pieces) SCC occurred more readily than the as-received material, in agreement with the findings in CERT, but the stress dependence was the same for the as-received alloys, as seen from the parallel curves in Figure 7. In our work, so far, one test has shown SCC at a stress level below the yield point in as-received material, and is an initial answer to the important question whether the quantitative equation can be applied to stresses below the yield point. More work is underway at one more lower stress level than reported here.

Future Work:

It is intended to combine the CERT data with the U-bend and or constant load results in one equation for translating exposure under known operating conditions into future performance, taking into account the spread to be expected within extrapolations.

Since cold work is an important parameter in accelerating SCC, although it is obviously not a prerequisite for cracking to occur, it is being examined in more detail. In practice, tubing is shaped, e.g., into U-bends, rolled into tube sheets, straightened without subsequent annealing during manufacture, and there are certain to be many other sources of residual stresses. Little is known about the influence of the degree of cold work on SCC, and for this reason it is included in the present BNL program. We are comparing the as-received condition with 5, 10, and 20% cold work in tests that include direct load and CERT. Environments include pure deaerated water as well as oxygen-free simulated primary and secondary water.

Capsule tests in which deformation simulating denting at tube support plate intersections, as well as tests in which cyclic stresses are applied to the specimens are due to resume in the near future.

Experiments are needed to examine an observation in limited tests in our work where some heats cracked readily as U-bends but were unexpectedly resistant in the CERT and/or constant load test. The cases so far encountered involved heats in the carbon range of 0.03% and up. It is intended to examine first the effects of more complex stresses than are found in simple tensile configurations such as were used in the CERT and constant load experiments.

Heat Treatment:

Attempts have been made during the past two years to generate our own susceptible heats of Inconel by means of high temperature annealing of heavily cold worked alloy 600. Annealing temperatures were chosen to simulate those that may possibly exist in tube mills. Earlier work(1) had indicated very limited success in the temperature range of about 1600°F to 1850°F (approximately 870°C to 1,000°C), for times ranging from 15 to 30 minutes. In more recent work, the material has been held at an annealing temperature for shorter times, and it was possible to obtain SCC susceptibility in an 0.03% carbon alloy by holding at temperature for about 1 1/2 to 2 minutes. At shorter or longer times than this we did not achieve susceptibility, as determined in CERT (by the presence of cracks and a maximum loss of ductility at 365°C in pure deaerated water) and also in U-bend tests (where cracking occurred only in the specimens that had been heated for about 2 minutes) as shown in Figure 9. These results may only apply to the heat that we used and it is not suggested that the specific temperature-time combination would be generally applicable to any other heat.

Structure:

The various heats of mill annealed alloy 600 tubing used in this program are typical of nuclear grade production; however, only about half of these heats have shown evidence of intergranular SCC when U-bend specimens were exposed to pure deaerated water at high temperatures. It is difficult to establish what differences exist between these heats that account for the fact that some are susceptible while others appear to be immune. A susceptible structure is generally associated with carbide-free grain boundaries, while semi-continuous grain boundary precipitates are beneficial in preventing SCC in caustic and pure water environments. Electrolytic etching in phosphoric acid showed earlier that all of the materials used in this program were relatively free of carbide precipitates in the grain boundary regions. The susceptibility of this alloy, therefore, cannot be judged on microstructural analysis alone. Small variations in processing history which occur within a mill or different mills must play an important role, and could account for the lack of clear and reproducible microstructural differences between resistant and susceptible heats.

Additional work on U-bends from this series will be done to examine grain boundaries by extraction replicas.

Remarks on H_2 Effects:

A definite accelerating effect of H_2 was observed on SCC in high temperature water in CERT, U-bends as well as tensile specimens. In the latter case, one heat (#11, 0.03%C) of commercially produced tubing did not crack in the as-received surface condition in pure water at 365°C in the CERT test as well as U-bends - although a basic tendency towards cracking was found in U-bends that were first pickled in HNO_3/HF. When tested as-received (resistant in water at 365°C) in CERT at 365°C in $H_2O + H_2$, intergranular SCC occurred.

Confirmation of this H_2 effect has now been found from a comparison of 9 heats tested in pure H_2O and $H_2O + H_2$ as U-bends at 365°C. In water alone, as shown in Table 3, only 2% failures occurred in 12 weeks, compared to 83% in $H_2O + H_2$.

CONCLUSIONS

Tentative conclusions to date:

1. Based on limited high temperature data, there seems to be a relationship between carbon content and activation energy for SCC of alloy 600 U-bends. More data are due at lower temperatures.

2. CERT data show a family of curves in a consistent set of Arrhenius plots, where the slope is about 33 Kcal/mole. Differences in crack growth rates appear due to changes in position of parallel curves.

3. H_2 in pure water causes more severe SCC than in water alone.

4. Confirmation of the beneficial effects of treating at 700°C for 15-20 hours has been found.

5. Cold work is adverse to SCC resistance in deaerated high temperature water.

6. Simulated final "mill annealing" for short periods (at about 1700-1775°F i.e. about 925-970°C) resulted in susceptibility to SCC.

7. Constant load tests indicated a failure time proportional to the fourth power of the inverse of applied stress.

Acknowledgements

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5. G. P. Airey, "Carbide Dissolution and Precipitation Kinetics of Inconel 600," EPRI Topical Report NP-2093, 1981.

TABLE 1 - Mechanical Properties and Chemical Composition of Materials

Material Identification	Ultimate Strength MPa	Yield Point MPa	Elongation %	Rockwell Hardness	Chemical Analysis										
					C	Mn	Al	S	Si	Ni	Cr	Ti	Cu	Fe	Co
Tubing Heat #2	717.1	386.3	39	R_B86	0.05	0.28	0.19	0.003	0.24	73.94	15.69	0.20	0.33	9.47	0.05
Tubing Heat #4	629.7	322.7	48	R_B79-82	0.01	0.26		0.004	0.10	76.74	15.10		0.21	7.56	
Tubing Heat #5	649.3	379.5	44	R_B83.5	0.01	0.28		0.006	0.08	75.59	15.76		0.31	7.94	
Tubing Heat #6 (unannealed)					0.29	0.28		0.003	0.20	75.40	15.78		0.01	7.99	0.045
Tubing Heat #10	683.1	331.9	45.5	R_B79	0.02	0.30	0.32	0.0006	0.14	75.95	15.17	0.28	0.22	8.19	0.84
Tubing Heat #11	669.5	352.3	42.5	R_B83	0.03	0.30	0.17	0.004	0.18	74.64	15.18	0.17	0.34	9.33	0.04

Heat #5 with 40% cold work

Table 2

Tentative Calculated Failure Times for Lab. U-Bend SCC

	Projected Weeks at:	
%C	315°C	290°C
0.05	150	1500
0.03	120	700
0.02	30*	150*
0.01	80	240

*Exceeded by ongoing tests, without visible SCC.

Table 3

Effect of the Presence of H_2 in H_2O at 365°C

Test duration: 12 weeks
Test medium: Pure, deaerated water (with and without H_2)
Test temperature: 365°C
Test specimens: U-bends
Heats: 9

RESULTS

	Cracked	# Tested	% Failed
Pure H_2O	1	45	2
Pure H_2 + H_2O	15	18	83

(H_2 = amount found in primary H_2O).

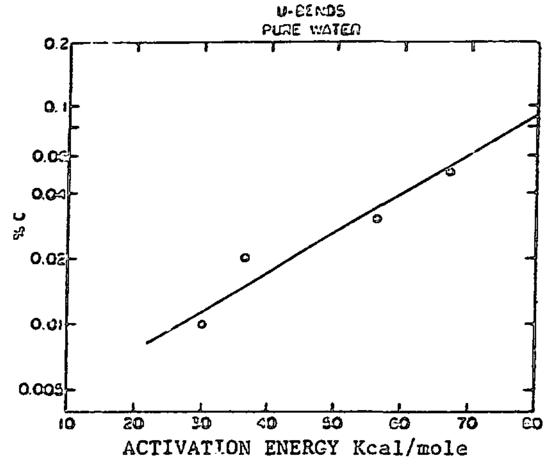


Fig. 1 - Tentative Activation Energies (Based on higher Temperature data)

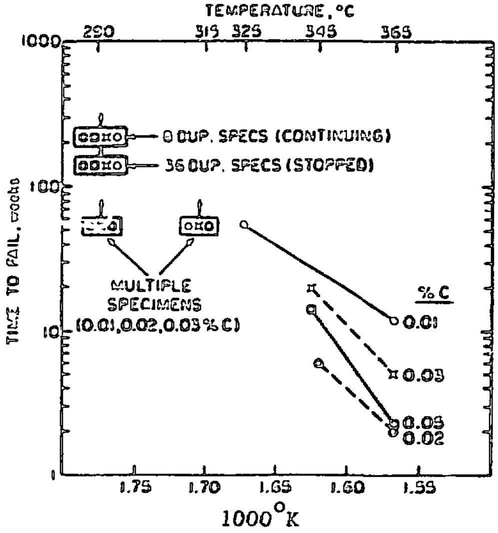


Fig. 2 - SCC in Pure Water U-Bends of commercial tubing

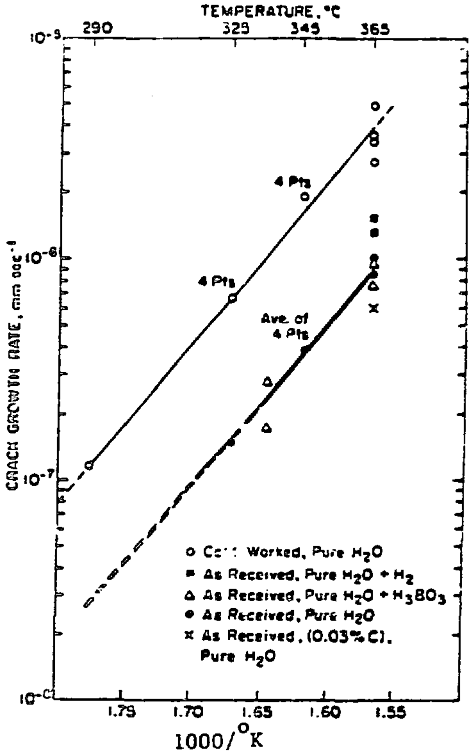
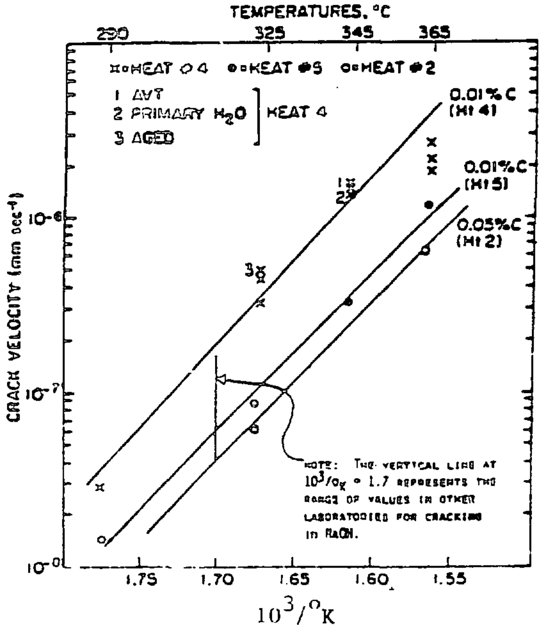


Fig. 3 - Crack Growth Rates, CERT Experiments 0.01%C



NOTE: THE VERTICAL LINE AT $10^3/°K$ = 1.7 REPRESENTS THE RANGE OF VALUES IN OTHER LABORATORIES FOR CRACKING IN NaOH.

Fig. 4 - Effect of Temperature on Crack Velocities Determined Using Cold Worked Inconel in CERT.

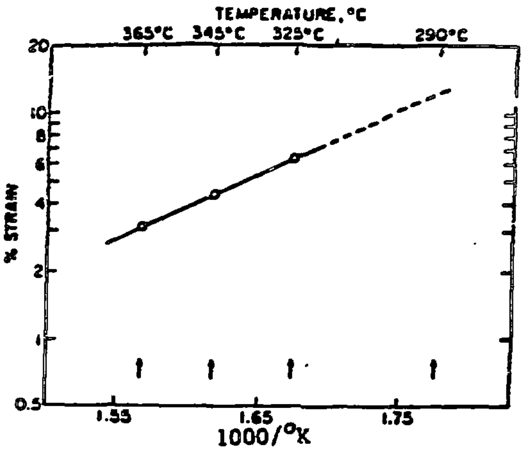


Fig. 5 - Extrapolation of SCC Initiation Strain Values from Fig. 3.

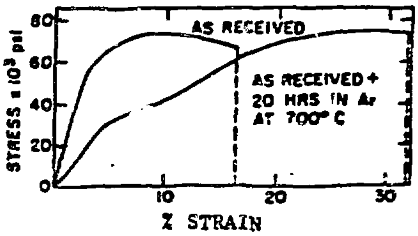


Fig. 6 - Comparison of Stress Strain Curves for Heat #2 with and without Heat Treatment at 700°C for 20 hours.

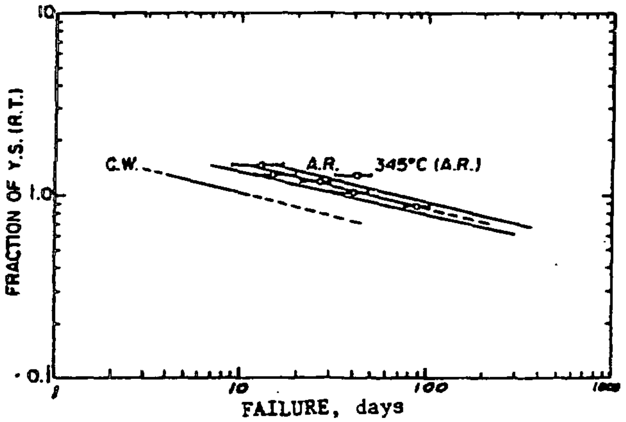


Fig. 7 - Failure Time vs. Stress. Constant Load in Pure H_2O. 365°C

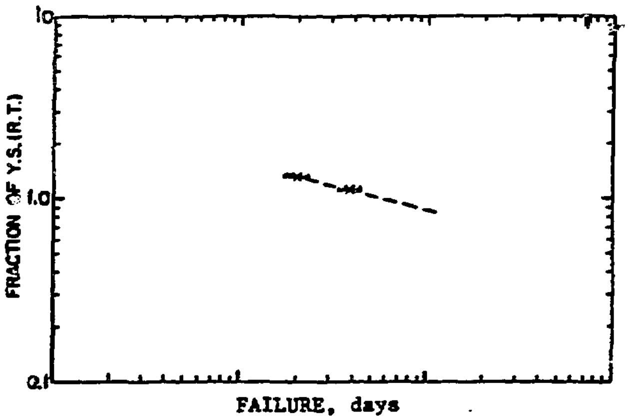


Fig. 8 - Failure Time vs. Stress. Constant Load in Simulated Primary H_2O. 365°C

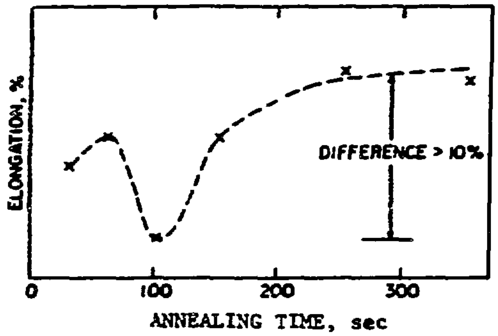


Fig. 9 - CERT Test: Annealing Response of Cold Worked 0.03%C Alloy 600 in the Range 1700°F to 1775°F, in pure H_2O Deaerated at 365°C.

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