MASTER

ELASTIC AND PLASTIC STRAINS
AND THE STRESS CORROSION CRACKING
OF AUSTENITIC STAINLESS STEELS

Progress Report
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ABSTRACT

Homogeneous deformation of type 310 austenitic stainless steel only slightly influenced the corrosion potential in a boiling 3% NaCl aqueous environment. The difference in a deaerated solution was of the order of 25 millivolts and somewhat more for an aerated solution. Elastic strains appeared to have little or no influence on the corrosion potential for fully annealed as well as 10% and 25% homogeneously deformed 310 steel.

Oxygen in the environment shifted the corrosion potential several hundred millivolts in the less active direction, as expected.

The critical cracking potential in a deaerated 3% NaCl solution was approximately the same for the annealed and homogeneously deformed specimens at approximately -125 mv SCE.

Introduction

The major effort in this initial period has involved the usual problems of getting a new program off the ground, including such items as building or adapting specialized equipment, gathering materials, educating new graduate students, etc. A case in point involves the 301 type transformable austenitic stainless steel. The material was received from the vendor labeled as 301 but actually was 304 and did not have the appropriate transformation characteristics. Although there will be no loss of funds since the error is being corrected without charge, the loss in time is irreparable.

This progress report essentially covers the determination of the influence of homogeneous deformation in a 310 non-transforming type of austenitic stainless steel. The particular parameters examined were the influence of stress (elastic strain) on the open circuit potential (E_{oc}), the effect of plastic strain in the environment on E_{oc} , the influence of oxygen on E_{oc} , the time to fail as a function of potential for the deformed conditions indicating the potential range for the critical cracking potential.

Materials and Methods

Type 310 austenitic stainless steel was received in the fully annealed condition in the form of .025" thick sheet. In this condition it had a 0.2% offset yield strength of 29,000 psi. Its composition is given in Table 1, below:

Table 1

<u>Cr</u>	<u>Ni</u>	<u>Mn</u>	<u>C</u>	<u>Mo</u>	<u>N</u>	<u>Si</u>	<u>Cu</u>
24.57	19.68	1.62	.055	.22	.017	.52	.25

One-half inch wide sheet specimens were homogeneously strained 10 and 25 percent elongation in the Instron. Homogeneity of the deformation was ensured by taking a length to width ratio of 20, where ASTM standards require only that the length to width ratio be no less than 4. From these homogeneously deformed strips, the two types of specimens shown in Fig. 1 were prepared. Type A specimens were employed for the time-to-fail tests and type B for the open circuit potential and oxygen studies.

Special constant load lever arm type of tensile machines were designed and built at C.W.R.U. Two views of the set-up are shown in the photographs of Fig. 2. Both units have the capability of applying stresses of approximately 200,000 psi on the types of specimens shown in Fig. 1 or on any type of

wire specimens that may possibly be introduced later. The environment cells provided for the transmission of the stress through a friction free slot which deters the escape of the hot or boiling aqueous environment. Reflux condensers provided for no loss of the environment or change in its concentration. In addition, it was necessary to have vapor-tight joints in the top to allow also for the insertion of the counter electrode, the reference electrode, introduction of air, oxygen, nitrogen, or any other gas, electrical connections, etc. Heating the aqueous environment was very simply and efficiently accomplished by several turns of heating "tape" controlled with variacs.

The environment was a 3 percent aqueous solution of NaCl made up with distilled water and HP grade salt. At ambient temperature the pH of this solution was 6.5-7.0, essentially neutral.

The potentials were applied and measured by Wenking potentiostats capable of measuring to approximately ± 5 millivolts for the potential ranges of interest. All potentials are reported with respect to the standard calomel electrode.

In all potential measurements, it is universally observed that initially the potential will drift in the more active direction. Eventually this drift will diminish and the potential will settle at some more or less steady state. The customary procedure is to take some arbitrary time such

as 1 or 2 hours, where the potential seems to be settling down and employ this throughout the investigation. This procedure was adopted here.

Results and Conclusions

It is well appreciated that cold work will increase the strength of austenitic stainless steels. This is true for homogeneous as well as heterogeneous deformation. The change in the 0.2% offset yield strength for 310 at ambient temperature is shown in Table 2, below:

Table 2

Yield Strength - Homogeneously Deformed

No deformation	yield strength	29,000 psi
10% elongation	" "	63,000 psi
25% elongation	" "	90,000 psi

It can be assumed that the change in Y.S. between ambient and 100°C is negligible in terms of our study.

The open circuit (E_{oc}) or rest potential was examined for the fully annealed and the two deformed states in the 3% NaCl solution at ambient temperature. All specimens were stressed up to the elastic limits and also loaded slightly

beyond to produce plastic flow while in the environment.

Also for each condition the influence of oxygen was evaluated by continuous deaeration as well as aeration of the environment during the test. The results are summarized in Table 3 which follows.

Table 3Open Circuit Potential (E_{oc}) vs. StressAmbient Temperature0 Percent DeformationDeaerated

No stress	-286 mv
All applied stresses up to 28 ksi	-286 mv

Aerated

No stress	-125 mv
All applied stresses up to 28 ksi	-125 mv

10 Percent DeformationDeaerated

No stress	-270 mv
All applied stresses up to 63 ksi	-270 mv

Aerated

No stress	-125 mv
All applied stresses up to 63 ksi	-146 mv

25 Percent DeformationDeaerated

No stress	-308 mv
All applied stresses up to 90 ksi	-308 mv

Aerated

No stress	-160 mv
All applied stresses up to 90 ksi	-184 mv

An examination of Table 3, clearly indicates elastic strains have no influence on the corrosion or open circuit potential (E_{oc}) for all conditions except perhaps for the aerated 10 and 25 percent homogeneously deformed specimens. Considering the inherent scatter in corrosion potential determinations, it is not possible, at this time, to unequivocally conclude that the approximate 25 mv change in the more active direction is real, although the direction of change is what one might anticipate. The proposed further studies such as with rolled and/or transformed steels should help to clarify this.

In addition, there does appear to be an influence of deformation on E_{oc} , particularly between the 0% or 10% deformation and the 25% deformation in the aerated condition. Here again, the proposed further tests should provide more insight to the phenomenon.

In all cases shown in Table 3, when the load was increased above the indicated yield strength values, there was an instant and substantial change of E_{oc} in the more active direction. With no further increase in load or removal of the load, the potential gradually (30-90 min.) drifted back to the original E_{oc} shown in the table. This is not a new phenomenon and has been reported in the literature, perhaps for a different set of circumstances, but essentially the same general phenomenon. Briefly, it has been rationalized

as a "break" in the protective surface and its subsequent repair with time. Since this is somewhat outside the scope of our immediate objectives, it will not be further considered.

The general independence of E_{oc} on elastic strains also indicates the inadequacy of the anodic dissolution mechanism for SCC. It is well established that elastic strains do influence the failure characteristics, and the anodic dissolution concept requires corrosion, but since the corrosion potential (E_{oc}) is not influenced by stress, there appears to be no relation between SCC and anodic dissolution. The anodic dissolution concept, although somewhat falling into disfavor still has a number of active adherents.

The influence of oxygen on E_{oc} is markedly evident in Table 3 for all conditions of deformation. Apparently, aeration of the environment moved the corrosion potential approximately 150 mv in the more noble (less active) direction. To be sure, for an active-passive material such as austenitic stainless steel one expects greater passivity in the presence of air (oxygen) than in its absence. However, it is significant to note that the potential shift was approximately the same for the homogeneously deformed as for the fully annealed specimens. It will be of interest to see if this holds true for the heterogeneously and transformation deformed steels.

The time-to-fail characteristics as a function of potential in the deaerated environment at 100°C are summarized in Figs. 3, 4, and 5. The applied stress was 90-95% of the yield strength for each condition. In all cases, with or without deformation, there was failure at anodic potentials and currents and no failure at cathodic conditions. All failures exhibited pitting at the anodic potentials which became more severe at the higher anodic potentials and no pits were observed at the cathodic potentials.

Obviously as the critical cracking potential (E_c) is approached the times-to-fail become increasingly long, and, of course, at some potential the time-to-fail becomes "infinite" (E_c). This places a somewhat practical burden on the precise pinpointing of E_c as is evident in the Figures indicating test times well in excess of 100 hours. The accuracy of the determination is simply a matter of the time necessary to closely bracket the E_c between fail and no-fail tests.

Although the critical cracking potential has not yet been pinpointed as well as desired, several significant observations can be made. It is apparent from Figs. 3-5, that the critical cracking potential and the corrosion potential (E_{oc}) have no direct relation with each other for both the undeformed and deformed conditions. Indeed, E_c is several hundred or more millivolts less active than E_{oc} . Again,

this would tend to discredit any SCC mechanism dependent upon anodic dissolution.

That E_c and E_{oc} are not the same potential has been observed for 304 stainless steel, fully annealed and in a boiling concentrated Mg_2Cl environment at temperatures near 130-140°C. However, these are the first data under circumstances involving a direct comparison between annealed and cold worked strengthened stainless steels and also for NaCl.

Of the greatest interest at the moment is the indication that the critical cracking potential for both undeformed and deformed specimens is about the same, approximately -125 mv. As indicated before, the E_c has not been pinpointed as closely as desired and thus the -125 mv value is only approximate. However, it is most important to extend this study to examine the influence on the critical cracking potential (E_c) of the structural variables as well as other parameters such as oxygen, temperature and pH. This aspect of the original three-year program which will be pursued (see proposal) should provide some insight to the nature of the deleterious influence of the chloride ion which appears to be an unique common denominator.

Finally, as indicated on Figs. 3-5, the corrosion potential (E_{oc}) varied from -450 to -500 mv for the deaerated environment at 100°C. A comparison of these values with those in Table 3 also for deaerated conditions but at ambient

temperatures indicated that the higher temperature shifted the E_{oc} several hundred millivolts in the more active direction, in line with anticipated normal behavior.

TIME OF PRINCIPAL INVESTIGATOR

The principal investigator, since the beginning of this agreement has spent approximately 25 percent of his time during the academic year and 30 percent during the summer. No change is expected for the remainder of the agreement or for any future one.

A. REST POTENTIAL VS. LOAD

B. STRESS CORR. CRACK.

FIG. 1: SPECIMENS

Figure 2: Cantilever Beam Type
Test Fixture for Time-to-Fail Tests
Showing Auxiliary Equipment.

FIG. 3: STRESS CORROSION CRACKING OF TYPE 310 S. S.
DEFORMED 0% (AS ANNEALED). DEAERATED 3% NaCl, 100° C.

FIG. 4: STRESS CORROSION CRACKING OF TYPE 310 S. S.
DEFORMED 10% UNIAXIALLY. DEAERATED 3% NaCl, 100° C.

FIG. 5: STRESS CORROSION CRACKING OF TYPE 310 S. S.
DEFORMED 25% UNIAXIALLY. DEAERATED 3% NaCl, 100° C.