DOE/ER/10972--T1

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DE82 015263

First Annual Progress Report

The Influence of Nitrogen on the Sensitization, Corrosion, Mechanical,
and Microstructural Properties of Austenitic Stainless Steels

DOE Contract No. DE-AC02-81ER10972

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April 1982

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A. OVERALL PROJECT

Personnel. In addition to the Principal Investigators, Professors William A. T. Clark and Digby D. Macdonald, partial support on this contract has been given to:

a) Dr. K. Nishimoto, from the Department of Welding Engineering, Osaka University, Japan, who has been with the project since its beginning.

Dr. Nishimoto may extend his period at Ohio State to two years, and will be retained on the project if so, but will most likely have to return to Japan this autumn.

b) Miss J. Shao, a researcher from The People's Republic of China, who has come to Ohio State fully supported by The People's Republic, has worked on the project throughout at no charge to the budget.

c) Dr. A. Yoshitake, a fully-supported researcher from Kobuto, Ltd., Japan, has collaborated in the electrochemical studies, again at no charge to the project.

d) Dr. S. Pednekar left the Department for an industrial position in December 1980. His tasks on the project were assumed by Dr. Nishimoto.

Much of the credit for the successful start to the program can be attributed to the efforts of researchers whose salaries were not charged to the project. In order to sustain this level of activity it is important that there is no reduction in personnel. Accordingly, the 1982-83 budget includes stipends for two graduate students, the minimum number considered feasible to achieve the project goals for the coming year.

Report on Research Progress

During this first year of the project, the research effort has concentrated on the electrochemical aspects of the effect of nitrogen on austenitic steels. The status of all the individual project tasks will be outlined briefly, and then more detailed results of the electrochemical studies conducted so far reported.

1. Materials Preparation

Considerable effort during this first reporting period has gone into obtaining the necessary materials, and fabricating samples and equipment for the experiments. The task of preparing the master alloys, according to the scheme outlined in Section III-1 of the original proposal, was given to Crucible Incorporated Research Centre. The cast alloys have compositions shown in Table I, from which can be seen that the carbon level has been kept almost constant at 0.043-0.053^{w/o}, while the nitrogen content varies systematically from 0.04-0.25^{w/o}. The other elemental additions are also held at constant composition. From the as-received sheet specimens for the EPR and polarisation tests were machined in the workshop of the Physics Department at Ohio State. In addition, the pressure balanced silver/silver chloride electrodes used in the simulated BWR environment tests were fabricated. Details of a proposal to cast two additional heats of the alloy will be given in the section describing proposed research.

2. Microstructural Studies and Stacking Fault Energy Measurements

Although some preliminary microstructural studies have been carried out, the principal research effort in this first period has been directed towards collecting electrochemical data, and a detailed report of this aspect will be given in the next period. This area of the project requires the addition of a graduate student to work on it full-time, and will also be stimulated by the planned installation of new analytical electron microscope facilities at OSU in Autumn 1982.

As explained in the proposed research, the results obtained from the electrochemical studies provide a number of hypotheses to explain the effect of nitrogen on sensitisation, and the microstructural studies will be an essential element in evaluating these.

3. Corrosion Studies

The following report outlines the work conducted to date on this aspect of the project, and indicates the substantial amount of data obtained so far.

ELECTROCHEMICAL STUDIES OF THE EFFECT OF NITROGEN ON THE CORROSION AND MECHANICAL PROPERTIES OF AUSTENITIC STAINLESS STEELS

by

K. Nishimoto, J. Shao, A. Yoshitake,
W.A.T. Clark, and D. D. Macdonald

I. General Objective

The aim of this study is to develop a systematic understanding of the effect of nitrogen on the corrosion, mechanical, and microstructural properties of austenitic stainless steels.

Nitrogen has been considered detrimental to the SCC behavior of stainless steels, especially in chloride environments.^(1,2) Recent investigations^(3,4) have, however, revealed that nitrogen additions of less than about 0.15 percent in austenitic stainless steels has no harmful effect on their SCC susceptibilities in high temperature water. Furthermore, it was reported that the TTS diagram for the intergranular corrosion of these steels is shifted in the retarding direction through nitrogen additions.⁽⁵⁾ This observation suggests that nitrogen should be a beneficial element with regards to the SCC behaviour in high temperature water because susceptibility to intergranular corrosion generally parallels that to stress corrosion cracking.

On the other hand, it is known that transgranular SCC is more frequently observed in the nitrogen-containing austenitic stainless steels than in the conventional ones when tested using the slow strain rate technique (SSRT).⁽⁶⁾ The mechanistic role of nitrogen in TGSCC is still unknown.

It is apparent from the above that the systematic study of the effects of nitrogen on the intergranular and stress corrosion cracking properties of

austenitic stainless steels is required in order to understand and predict the susceptibilities of these materials to SCC failure in corrosive environments. Accordingly, the effect of nitrogen on the SCC of austenitic stainless steels in high temperature water and the susceptibility of these alloys towards intergranular attack are being studied in the first phase of this project.

So far, the susceptibility to intergranular corrosion of nitrogen-containing 18Cr-8Ni stainless steels has been examined using a potentiostatic technique. The test adopted is the EPR test, which generally yields results that are in good agreement with the known susceptibilities of austenitic stainless steels to SCC in high temperature water environments which simulate Boiling Water Reactors.^(7,8) Polarization studies were carried out on a few steels in high temperature water containing 0.01 M Na_2SO_4 at 250°C in order to define their general corrosion behaviours.

2. Current Goals

The goals for this period were: 1) to study the effect of nitrogen on the sensitization of 18Cr-8Ni stainless steels containing nitrogen of 0.04, 0.10, 0.16, and 0.25 wt% (and carbon of about 0.05 wt%), using the EPR method, and 2) to obtain polarization curves in deaerated 0.01 M Na_2SO_4 solution at 250°C for few steels, in order to examine the influence of sensitization on corrosion in this environment.

3. Experimental Detail

The steels used were produced by laboratory-melting and were obtained from Crucible Inc.; their chemical compositions are listed in Table 1. These steels were forged and hot-rolled to 4x100x250 mm sheet stock. All the steels were heat-treated at 1050°C for 15 minutes as a solution treatment prior to each experiment. Solution annealing and longer sensitizing heat treatments were carried out in an

electric furnace under an argon atmosphere. Lead baths were used for specimens sensitized for short periods (less than 15 minutes) so as to obtain maximum heating rates. All the specimens were water quenched on removal from the furnace or the bath.

The degree of sensitization was determined by means of the EPR technique. This method requires the measurement of anodic polarization curves in deaerated 0.5 M Na_2SO_4 + 0.01 M KSCN solution at 30°C. To carry out this measurement, the potential was first scanned in the anodic direction, starting from the corrosion potential, held at 200 mV (vs SCE) for 2 minutes, and then scanned in the reverse direction, as shown schematically in Fig. 1. The voltage scan rate was 50mV/min. The activation ratio R_a , which is the parameter used to express the degree of sensitization of the steel, is the ratio of the maximum activation current to the critical passivation current. It has already been verified elsewhere^(7,8) that a good correlation is observed between R_a and the susceptibility to IGSCC in simulated BWR environments.

The polarization curves were measured for few steels in 0.01 M Na_2SO_4 at 250°C using the autoclave system shown in Fig. 2. The mixing and feed tanks, and all transmission tubing were constructed of Type 316 stainless steel, whereas the autoclaves themselves are made of titanium. The oxygen concentration in the feed water to the high pressure pump was monitored using a Beckman Model 735 oxygen analyser. The pressure in the system was set to 700 psig at 250°C in order to maintain a single liquid phase within the loop.

Details of the measurement cell used in this work are given in Fig. 3. This cell consists of the working electrode (specimen), the platinum counter electrode and an external reference electrode (in this case a silver/silver chloride [0.1 N KCl] electrode⁽⁹⁾). The test solution used was 0.01 N Na_2SO_4 , deaerated by argon purging. The polarization curves were measured within the potential

Table 1. Chemical Composition of Materials

Heat Number	Weight Percent									
	C	Mn	P	S	Si	Ni	Cr	Mo	Cu	N ₂
B-4	0.053	1.77	0.031	0.008	0.41	8.49	19.27	0.36	0.16	0.040
B-10	0.044	1.77	0.034	0.007	0.46	8.59	18.87	0.36	0.16	0.11
B-16	0.043	1.78	0.028	0.008	0.41	8.63	18.80	0.38	0.16	0.16
B-25	0.046	1.37	0.030	0.008	0.40	8.89	18.90	0.38	0.17	0.25

Fig. 1. Definition of the Activation Rate Ra in the EPR Technique.

Fig. 2. Autoclave Systems Used in the Experiments

Fig. 3. Design of the Cell Used for Measurements of Polarization Curves.

range -750 mV (SHE) to +500 mV (SHE), at a potential scan rate of 25 mV/min.

4. Results and Discussion

4.1 Effect of Nitrogen on Sensitization

To study the effect of nitrogen on sensitization resistance, solution annealed 15 mm square - 4 mm thick specimens of 18Cr-8Ni steels (containing about 0.05 wt% carbon and 0.04 to 0.25 wt% nitrogen) were heated for up to 170 hours at temperatures within the normal sensitization range (550 to 850°C) for austenitic stainless steels. The surfaces of the heat-treated specimens to be subjected to the EPR measurement were then finished by successive grinding through #600 SiC paper.

Figs. 4-7 show the R_a values obtained from the EPR tests, indicating the degree of sensitization as a function of the sensitizing time at each temperature. For heat treatment temperatures of 550, 650, and 750°C, R_a was found to increase with increasing time in all cases. This effect is most pronounced at 650°C. No increase in R_a with heating time was observed at 850°C. This indicates that the upper temperature limit for sensitization of these steels lies between 750°C and 850°C.

On the basis of these results, TTS diagrams were constructed by plotting points having equivalent R_a values, for each steel, as a function of time and temperature. Figs. 8-11 present TTS diagrams obtained for steels containing 0.04 to 0.25 wt% nitrogen. Nitrogen additions up to at least 0.16 wt% have the effect of retarding sensitization; that is, the time required to achieve a given degree of sensitization increases with increasing nitrogen content. The steel containing 0.25 wt% nitrogen was, however, less resistant to sensitization than the others. These results are in approximate agreement with metallographic investigations⁽⁵⁾ of sensitization in these steels.

Fig. 4. Relation Between Heat-Treating Time at 550°C and Ra, as Measured by the EPR Technique.

Fig. 5. Relation Between Heat-Treating Time at 650°C and Ra, as Measured by the EPR Technique.

Fig. 6. Relation Between Heat-Treating Time at 750°C and Ra, as Measured by the EPR Technique.

Fig. 7. Relation Between Heat-Treating Time at 850°C and Ra, as Measured by the EPR Technique.

Fig. 8. Effect of Heat Treatment Temperature and Time on Sensitization of B-4.

Fig. 9. Effect of Heat Treatment Temperature and Time on Sensitization of B-10.

Fig. 10. Effect of Heat Treatment Temperature and Time on Sensitization of B-16.

Fig. 11. Effect of Heat Treatment Temperature and Time on Sensitization of B-25

The role of nitrogen in retarding sensitization is of interest because nitrogen has been believed to be detrimental in that it may promote intergranular corrosion. Traditionally, this has been explained by a tendency to form Cr_2N at the grain boundaries, causing a chromium depleted zone along the grain boundaries, as does the precipitation of Cr_{23}C_6 in high carbon alloys.

The effect of nitrogen observed here might be accounted for by one of several mechanisms,⁽¹⁰⁾

- 1) Retardation of nucleation or growth of Cr_{23}C_6 .
- 2) Change in activity of chromium in equilibrium with Cr_{23}C_6 (i.e., chromium concentration adjacent grain boundaries).
- 3) Change in the ease of the passivation of the alloy, so that higher levels of chromium depletion are necessary for detection in the EPR test.

Insufficient work has yet been carried out to determine the most probable mechanism. However, according to the metallographical study conducted in this work, the retardation of sensitization by nitrogen additions is closely related to the precipitation behaviour at grain boundaries. Accordingly, for nitrogen concentrations of up to 0.16 percent, the time at which intergranular precipitates were first observed increases, and the density of the precipitates after a given time decreases with increasing nitrogen content. Conversely, a higher density of precipitates was observed in the 0.25 percent nitrogen steel than in the other alloys. This observation suggests that the nitrogen additions retard the precipitation of chromium carbide, but excess nitrogen causes a different precipitate to form at the grain boundaries (e.g., chromium nitride) which might itself give rise to intergranular corrosion. As a result, it is concluded that mechanism (1) is the most probable in this case. It is, however, not known how nitrogen affects the nucleation or rate of growth of carbides in these steels. These problems will

be investigated further in the next phase of the project.

4.2 Polarization Studies in High Temperature Water

Polarization curves were obtained for a few steels in 0.01 M Na_2SO_4 solution at 250°C, and are shown in Figs. 12 and 13. In both figures, the solid and dotted lines show, respectively, polarization curves of the solution annealed steels, and those for alloys which were sensitized at 650°C for two hours. In terms of the corrosion potential, no significant difference can be seen between these steels, i.e., they both lie between -660 and -670 mV (SHE). However, both the critical current density and the passive current are higher in the case of the sensitized steels than for the solution annealed materials. This implies that steels heated at 650°C for two hours are more susceptible to intergranular corrosion in this environment.

A transition region from passive to trans-passive behaviour exists in the range of -100 to +200 mV (SHE) for these steels. It is generally believed that in such a transition region the surface passive film is unstable, and IGSCC is liable to occur.⁽¹¹⁾ Accordingly, our future SSR tests on these alloys will be carried out under controlled electrochemical conditions at an applied potential of 0.0 mV (SHE).

5. Summary

- 1) Nitrogen additions of up to 0.16 wt% retard sensitization of 18Cr-8Ni austenitic stainless steels. However, nitrogen additions to levels above ~0.25 wt% promote sensitization.
- 2) The retardation of sensitization by nitrogen can possibly be explained as being due to retardation of the nucleation or rate of growth of chromium carbides.

3) Polarization studies in high temperature 0.01 M Na_2SO_4 solutions at 250°C demonstrate that the sensitized alloys are electrochemically more active than the solution annealed materials thereby indicating that they are susceptible to intergranular attack.

Fig. 12. Polarization Curves for Solution Annealed and Sensitized B-4 in 0.01 m Na_2SO_4 Aqueous Solution at 250°C .

Fig. 13. Polarization Curves for Solution Annealed and Sensitized B-16 in 0.01 mol Na_2SO_4 Aqueous Solution at 250°C .

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