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EFFECT OF THERMAL STABILIZATION ON THE LOW-TEMPERATURE STRESS-CORROSION CRACKING OF INCONEL 600

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ABSTRACT

The propensity to low-temperature stress-corrosion cracking (SCC) of thermally stabilized Inconel 600 in sulfur-bearing environments has been investigated using U-bends and slow-strain-rate testing. The results have been compared with those of sensitized Inconel 600. The potential dependence of crack-propagation rate has been established in a single test by using several U-bends held at different potentials, by choosing an appropriate electrical circuitry. The difference in SCC susceptibility of the sensitized and stabilized materials has been discussed in terms of the grain-boundary chromium depletion and resulting intergranular attack in boiling ferric sulfate-sulfuric acid tests, and electrochemical potentiokinetic reactivation (EPR) tests.

INTRODUCTION

Sensitized Inconel 600 suffers rapid stress corrosion cracking (SCC) at low temperature in sulfur bearing environments such as polythionic acid, sodium tetrathionate and sodium thiosulfate.¹⁻⁵ Scarberry et al.¹ reported maximum sensitization, i.e., maximum susceptibility to intergranular attack in nitric acid and SCC in polythionic acid when the alloy was exposed to times and temperatures near the boundaries of the precipitation region on the time-temperature-transformation diagram resulting in continuous grain boundary carbides with continuous chromium depleted areas near the boundaries. However, treatment of the alloy to conditions well within the precipitation region resulted in discontinuous grain boundary precipitation and replenishment of chromium depleted areas.

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As a result, propensity to intergranular corrosion in nitric acid and SCC in polythionic acid reduced significantly.

SCC resistance in caustic is also improved significantly by a suitable thermal treatment in the carbide precipitation regime⁶⁻¹⁰ and the improvement has been correlated with the presence of a semi-continuous grain boundary precipitate.¹¹ Such a thermal treatment also improves the SCC resistance in high temperature water.^{12,13} However, slow strain rate tests in high temperature water on thermally stabilized (as received + 700°C, 20h) specimens showed that although significant improvement in SCC resistance resulted from thermal stabilization, very shallow intergranular penetration was still observed on the surface of the specimen.¹³ Recently the grain boundary chromium depletion and the resulting intergranular corrosion and SCC behavior have been studied as a function of thermal treatment.^{14,15} For optimum thermal condition, Airey¹⁵ has suggested the following thermal treatment: 982-1010°C for 1 to 5 minutes, followed by 704°C for 15 hours. This heat treatment apparently provides the maximum resistance to SCC in caustic and also gives a relatively uniform condition of microstructure and mechanical properties and thus helps to overcome to a large extent the problem of dealing with the wide heat to heat variability of mill annealed materials. In this study, we have generally followed the above thermal treatment suggested by Airey.

In the present work we compare the SCC susceptibility of thermally stabilized Inconel 600 in polythionate environments, using both static and dynamic straining, with that of sensitized Inconel 600 that undergoes rapid SCC in this environment. Also, intergranular corrosion susceptibility of the stabilized and sensitized materials are compared using boiling ferric sulfate-sulfuric acid tests¹⁶ and electrochemical potentiokinetic reactivation (EPR) tests.^{17,18}

EXPERIMENTAL

Tests were conducted on commercially produced nuclear grade Alloy 600 material. Two different heats with compositions shown in Table 1 were used. Most of the tests were conducted on the tubing material (heat No. 1, Table 1) outside diameter 22 mm and wall thickness 1.24 mm. Some U-bend tests were performed with the 5 mm thick plate material (heat No. 2, Table 1). Heat No. 1 was sensitized to two different conditions - directly sensitized from the mill annealed condition (MAS), and solution annealed followed by sensitizing heat treatment (SAS). All heat treatments are described in detail in Table 2. Heat No. 2 was sensitized to SAS condition only. For thermal stabilization (TS), both materials received the same heat treatment: 982°C for 4 minutes, rapidly cooled in air followed by 705°C for 16 h.

Reverse U-bends were prepared from the tubing material (heat No. 1) using procedures described elsewhere.¹³ The plate material (heat No. 2) was cut into approximately 100 mm x 6 mm strips and formed into U-bends following ASTM standard G 30-72. All U-bend and slow strain rate tests were conducted in aerated solution of freshly prepared 0.1M sodium tetrathionate ($\text{Na}_2\text{S}_4\text{O}_6$), following procedures described elsewhere.^{4,5}

The U-bends prepared from the plate material were tested using a modification of the technique of Seys and Van Haute¹⁹ which allowed multiple specimens to be tested, each at a different potential, in a single test. This replaced their single wire specimen along which they created a potential gradient by means of an impressed current. In our test, several specimens were connected in series, separated by resistors of suitable predetermined values. The potential of one of the specimens was adjusted to a desired value by means of a potentiostat. A relatively large direct current (~ 0.2 A) was passed from a power supply through the circuit, thus bringing the potential of each specimen to a different value as a result of the (iR) potential drop across each of the resistors. The potential of each specimen was measured with a Luggin probe - calomel electrode combination. In the Seys and Van Haute technique, the resistance of the wire specimen was used to provide the iR drop.

For detecting susceptibility to intergranular attack, specimens of roughly 10 to 20 cm² area each were tested for 24 hours in a boiling solution of ferric sulfate and sulfuric acid following the appropriate ASTM standard.¹⁶ In each test, only a single specimen was used.

EPR tests were performed on 1 cm² coupons polished to 600 grit, in 0.5M H₂SO₄ + 0.01M KSCN solution. The method consisted of holding the specimen at +0.4V vs. SCE for 4 minutes and then polarizing it to -0.2V vs. SCE at a scan rate of 1 mV/S. A PAR Model 350 Corrosion Measurement System was used which automatically computed the amount of charge accumulated during the polarization.

RESULTS AND DISCUSSION

Potential-time Behavior of U-bends

The variation of corrosion potential with time of MAS and TS reverse U-bends (heat No. 1) in 0.1M sodium tetrathionate solution is shown in Figure 1. In both cases, the potential shifted to the negative direction within a few seconds of immersion, and then slowly drifted towards the positive direction. However, unlike the MAS specimen, the TS one had a sharp transition to positive potential within a few hours. The potential monitoring was discontinued after about 50 hours, except for occasional checks of the potential of the TS specimen which continued to move slowly in the positive direction and reached +312 mV vs. SCE in 150 hours. The MAS specimen suffered through wall cracking within about 5 to 6 hours of immersion, whereas the TS specimen did not crack in 800 hours. The potential excursions in Fig. 1 are perhaps indications of film formation and growth on the specimen surfaces and it is apparent that the two specimen surfaces behaved very differently, owing perhaps to different film composition on them. Also, the potential of the sensitized (MAS) specimen could have stayed low because of active grain boundary corrosion. It is evident from the above results that the SCC resistance of TS specimen to polythionate cracking improves significantly by the TS treatment.

Multiple U-bends Under Potential Control

Figure 2 shows the relationship between electrochemical potential and crack propagation rate of SAS U-bends of heat No. 2 material. An initial 20 h

test caused throughwall cracks in several specimens in the potential range where the propagation rate is very high. Therefore, a second test was conducted for about 7 hours at those potentials. After the test, each specimen surface was polished and examined under the microscope and the crack propagation rate was determined by dividing the maximum crack length by the total test duration and thus, it includes the initiation time involved in each case. Therefore, the net propagation rate will be higher in each case than that shown in Fig. 2. In addition, several tests were conducted using a single specimen each time, held potentiostatically at a particular potential and the results were essentially similar to those in Fig. 2. The results show that the SAS material cracks very rapidly in 0.1M tetrathionate over a wide range of potential. The specimen at +500 mV did not crack but suffered intergranular attack (IGA), as shown in Fig. 3.

Five TS U-bends, using heat No. 2 were also tested simultaneously in 0.1M tetrathionate solution within the potential band of -293 to +165 mV SCE. The test was continued for 100 hours without any cracks on any of the specimens.

The multiple specimen tests under potential control appears to be a very elegant method of SCC testing where susceptibility over a wide range of potential can be determined in a single test. The method has been applied successfully in SCC testing in high temperature environments and is currently being used for examining caustic cracking of Alloy 600.²⁰

Slow Strain Rate Testing

Four TS specimens tested with strain rates of 1, 2 and $5 \times 10^{-6}/s$ and $10^{-5}/s$ in 0.1M tetrathionate showed almost identical ultimate tensile stress (UTS) and % elongation to failure and these values were similar to those for a TS specimen tested in the laboratory air at $10^{-5}/s$ (Table 3). However, the specimens tested in the environment at 1 and $2 \times 10^{-6}/s$ showed a few extremely shallow intergranular penetrations on the faces of the specimens (Fig. 4). The specimens underwent considerable amount of necking and the SEM fractograph exhibited completely ductile behavior (Fig. 5).

Another specimen was held in 0.1M tetrathionate solution on a MTS servohydraulic machine under stroke control at an initial nominal stress of 262 MPa, i.e., σ_y yield strength of the material. The load relaxed owing to initial creep to about 236 MPa (nominal) within the first two days, but subsequently held relatively steady. After four weeks, the solution was replaced with a fresh batch and the specimen was strained to failure at a strain rate of $10^{-6}/s$. The results (specimen 3, Table 3) indicate some reduction in % elongation and a slight reduction in UTS compared to those strained in 0.1M tetrathionate immediately after immersion, or in laboratory air. However, the fractograph of specimen 3 was completely ductile. The reduction in % elongation or UTS in specimen 3 was probably due to some pitting that slowly occurred during the four weeks of exposure of the specimen in the tetrathionate solution and is not related to any intergranular penetration. The U-bends, tensile specimens and separate coupons of the TS material suffered localized deteriorations on the surface within a few weeks of immersion in the tetrathionate environment, as shown typically in Fig. 6(a) for a TS coupon immersed in 0.1M tetrathionate solution for two weeks.

There were some minute pits which grew larger with time, as illustrated in Fig. 6(b) for the same specimen examined eight weeks after immersion. It should be pointed out, however, that Inconel 600 would suffer some localized attack under any thermal condition in the severe environment tested. However, from the SCC standpoint, these pits did not lead to any premature failure of the TS specimen, as observed from the results on specimen 3 (Table 3). The SAS specimen, however, when tested as above, i.e., held for a few weeks on the MTS machine and then slowly strained, suffered severe SCC with a % elongation and UTS of 6% and 253 MPa respectively, and an average crack propagation rate of 50 nm/s, based on the maximum crack length and the total time of the slow strain rate test.

Susceptibility to Intergranular Attack

Ferric Sulfate - Sulfuric Acid Test

The results of 24 h tests in boiling solutions of the above environment for mill annealed (MA), MAS, SAS and TS materials of heat No. 1 are summarized in Table 4. Evidently, the sensitizing heat treatments increased the susceptibility to intergranular attack significantly, the effect of SAS treatment being much more severe than the MAS one. Clearly, the TS treatment reduced the susceptibility to intergranular attack substantially, the weight loss being smaller by about a factor of 3.5 than that for the MA material. All four specimens were bent in a vice (~ 30 to 45°) after the tests and the resulting SEM micrographs (Figs. 7(a) to (c)) for the MA, MAS and TS specimens respectively show that all of them suffered cracking as a result of the bending. The SAS specimen almost disintegrated in the environment, as was also noticed by Theus²¹ for this type of material in this environment. Lacking any appreciable grain boundary strength, the SAS material became very soft and deformed readily when bent and gave a ductile appearance in the SEM micrograph, Fig. 7(d). The major implication of the above tests is that the TS material, in spite of significant improvement in weight loss in the ferric sulfate-sulfuric acid environment, still shows some susceptibility to intergranular attack.

EPR Tests

The results of the EPR tests, expressed as the integral charge value normalized to the grain boundary area are shown as $P_a(\text{C/cm}^2)^{17}$ in Table 4 for the MA, MAS, SAS and TS materials of heat No. 1, where,

$$P_a(\text{C/cm}^2) = \frac{Q}{\text{GBA}}$$

and

Q = charge measured during the polarization scan,

$$\text{GBA} = A_s (5.09544 \times 10^{-3} \exp(0.34696 X)),$$

A_s and X being the specimen area and ASTM grain size at a magnification of 100 respectively. It is clear from the P_a values in Table 4 that the EPR tests

make good distinction between the MAS and SAS specimens, but the difference between the MA and TS specimens is small. Sensitization increases the potential range for active dissolution during the reverse scan, as can be seen from the polarization curves in Fig. 8 for the four heats tested, and thus accounts for the higher P_a values for the sensitized specimens. In sensitized stainless steel, EPR tests apparently saturate at higher levels of sensitization, causing a loss of discriminating power.²² However, this aspect of sensitization of Inconel 600 was not studied by us.

The relatively large P_a values reported in Table 4 for all four heats are due to the comparatively slower scan rate (1 mV/s) used in our tests, compared to those generally used for sensitized stainless steels.^{17,22} However, for a comparative evaluation of the four heats, the scan rate chosen should not influence the results. Future work will involve examining the effects of scan rate, and also of environments containing much lower concentrations of KSCN which apparently provide better separation of results in Inconel 600.²³

Sensitized Inconel 600 seems to give a much larger P_a value compared to that of sensitized 304 stainless steel. For example, SAS 304 stainless steel which also suffers rapid cracking in the tetrathionate environment, gave a P_a value of 109.5 C/cm² after the EPR test in 0.5M H₂SO₄ + 0.01M KSCN at a scan rate of 1mV/S, compared to a P_a value of 774.3 C/cm² for SAS Inconel 600 (Table 4). The higher P_a value for Inconel 600 is mainly due to two factors: (a) carbon solubility in Inconel 600 is much less than in 304 stainless steel and hence Inconel 600 is amenable to more severe sensitization, and (b) owing to the lower chromium content of Inconel 600, its matrix is generally attacked much more than in the 304 stainless steel by the environment during the EPR test. The high P_a value of 133.2 C/cm² for the TS specimen in our EPR test is perhaps due to the second factor.

Figures 9(a) to (d) illustrate the optical micrographs for the MA, MAS, SAS and TS specimens after the EPR tests. Clearly both MAS and SAS specimens were significantly attacked, with the grain boundary grooves in the SAS being somewhat more continuous than those in the MAS material. The MA specimen also appears to be slightly attacked, while the nature of attack on the TS material remains rather unclear. SEM micrographs on the four specimens, especially the MA and TS ones did not provide any additional information.

Transmission Electron Microscopy

In order to follow the grain boundary carbide precipitation, thin foils of the MA, MAS, SAS and TS materials were examined under the transmission electron microscope. The MA material appears to have some grain boundary areas free from any carbide precipitation, Fig. 10(a), and some areas with relatively large inter and intra granular carbide precipitates, Fig. 10(b). The MAS and SAS treatments cause much more continuous carbide precipitation along the boundaries, Figs. 10(c) and (d) respectively, the width of the precipitates being much larger in the SAS material. The TS treatment gives rise to semi-continuous carbide precipitates, Fig. 10(e), as was also observed by others.^{14,24} No attempt was made to obtain a quantitative evaluation of chromium depletion or segregation of other elements such as phosphorus and sulfur as

a result of the various heat treatments. However, Airey mentions^{15,24} that for the TS heat treatment chosen in this study, chromium re-diffusion generally becomes complete in about 10 hours at 705°C.

CONCLUSIONS

(1) The TS treatment significantly improves the resistance to polythionate SCC of Alloy 600 in both static and dynamic straining tests.

(2) The potential dependence of crack propagation rate has been established in a single static test holding several U-bends at different potentials, using a modification of the Seys and Van Haute technique.

(3) Weight loss results of boiling ferric sulfate-sulfuric acid tests give a reliable quantitative correlation of the susceptibility to intergranular attack resulting from sensitizing or stabilizing heat treatments.

(4) Results of EPR tests seem to be confirmative for sensitized specimens, but rather inconclusive for the TS material.

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TABLE 1

Chemical Composition (wt.%) of Alloy 600 Tubing and Plate

Heat No.	Cr	Fe	C	Cu	Si	Al	Ti	Mn	Co	S	Ni
1 (Tubing)	14.62	9.41	0.04	0.40	0.32	0.29	0.22	0.17	0.02	0.001	balance
2 (Plate)	14.57	9.04	0.05	0.29	0.07			0.25		0.004	balance

TABLE 2

Heat Treatment and Symbols Used

MA - Mill annealed (As received)

MAS - MA + 621°C, 18 h

SAS - 1135°C, 45 min., water quenched + 621°C, 18 h

TS - 928°C, 4 min., rapidly air cooled + 705°C, 16 h

TABLE 3

Results of Slow Strain Rate Tests on TS Specimens
in 0.1M Tetrathionate Solution*

Specimen No.*	Strain Rate	% Elongation to Failure	UTS, MPa
1	$10^{-5}/s$	46	640
2	$10^{-6}/s$	44	640
3	$10^{-6}/s$	36	617

*Specimen 1 was tested in laboratory air, 2 in 0.1M tetrathionate solution, immediately after immersion, 3 was held in 0.1M tetrathionate solution on a MTS machine under stroke control at an initial nominal stress of 262 MPa for 4 weeks and then slowly strained at $10^{-6}/s$ in a fresh solution of 0.1M tetrathionate.

TABLE 4

Results of Ferric Sulfate-Sulfuric Acid Test and
EPR Tests on Four Different Specimen Types

Specimen Type	Weight Loss in Ferric Sulfate-Sulfuric Acid Test, mm/y	P _a Values From EPR Tests, C/cm ²
MA	4.45	111.3
MAS	41.55	209.4
SAS	95.66	774.3
TS	1.29	133.2

Fig. 1. Potential-time behaviour of U-bends of sensitized (MAS) and thermally stabilized (TS) Inconel 600 in 0.1M sodium tetrathionate solution.

Fig. 2. Relationship between potential and crack propagation rate of sensitized (SAS) Inconel 600 in 0.1M tetrathionate solution. Specimens were multiple U-bends held at different potentials.

Fig. 3. Intergranular attack on sensitized (SAS) Inconel 600 U-bend held at +500 mV vs. SCE in 0.1M tetrathionate

Fig. 4. Shallow intergranular penetration on the face of tensile specimen of stabilized (TS) Inconel 600 tested at a strain rate of 10^{-6} /s in 0.1M tetrathionate solution. 1000x

Fig. 5. Typical SEM fractograph of stabilized (TS) Inconel 600 tensile specimen after slow strain rate test in 0.1M tetrathionate solution. 1000x

Fig. 6(a). Localized attack on a stabilized (TS) Inconel 600 coupon immersed for 2 weeks in 0.1M tetrathionate solution. 100x

Fig. 7(a). SEM micrograph of a mill annealed Inconel 600 specimen tested in boiling ferric sulfate and sulfuric acid and bent after the test. 100x

Fig. 6(b). Pitting on the same specimen as in Figure 6(a) after 8 weeks. 100x

Fig. 7(b). Same test as in Fig. 7(a) on a mill annealed and sensitized (MAS) Inconel 600 specimen. 500x

Fig. 7(c). Same test as in Fig. 7(a) on a stabilized (TS) Inconel 600 specimen. 1000x

Fig. 8. Reverse scan polarization test (EPR) on Inconel 600 under four different thermal conditions in 0.5M H₂SO₄ +0.01M KSCN solution at a scan rate of 1 mV/S.

Fig. 7(d). Same test as in Fig. 7(a) on a solution annealed and sensitized (SAS) Inconel 600 specimen. 500x

Fig. 9(a). Optical micrograph of a mill annealed (MA) specimen after EPR test. 400x

Fig. 9(b). Optical micrograph of a mill annealed and sensitized (MAS) specimen after EPR test. 400x

Fig. 9(d). Optical micrograph of a stabilized (TS) specimen after EPR test. 400x

Fig. 9(c). Optical micrograph of a solution annealed and sensitized (SAS) specimen after EPR test. 400x

Fig. 10(a). Transmission electron micrograph (TEM) of a mill annealed (MA) specimen showing relatively clean grain boundary areas.

Fig. 10(b). TEM of a mill annealed specimen (MA) showing inter and intra granular precipitates.

Fig. 10(d). TEM of a solution annealed and sensitized specimen (SAS) showing heavy continuous grain boundary precipitates.

Fig. 10(c). TEM of a mill annealed and sensitized (MAS) specimen showing relatively fine but continuous grain boundary precipitates.

Fig. 10(e). TEM of a thermally stabilized (TS) specimen showing semi-continuous grain boundary precipitates.