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〈研究論文〉

# INTERGRANULAR CORROSION TEST METHODS FOR TYPE 430 STAINLESS STEEL

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## ABSTRACT

Several testing methods for determining intergranular corrosion properties of Type 430 stainless steel are described. These include a new electrochemical potentiokinetic reactivation (EPR) test, a chemical etching test, and modified immersion tests from the ferric sulfate-sulfuric acid and cupric sulfate-sulfuric acid tests. A good agreement was observed between the tests. The tests described in this paper can be utilized for both heat treated and welded samples.

## INTRODUCTION

Intergranular corrosion is a type of localized attack at and adjacent to grain boundaries, with relatively little corrosion of grains. Intergranular corrosion can be caused by impurities at the grain boundaries, enrichment of one of the alloying elements, or depletion of one of these elements in the grain boundary areas. In stainless steels, it is usually caused by the preferential dissolution of chromium depleted zones adjacent to grain boundaries. In austenitic stainless steels these chromium depleted zones are developed when the alloys are exposed to a temperature between 482°C (900°F) and 816°C (1,500°F). In this temperature range, chromium carbides (or carbonitrides) precipitate

near grain boundary resulting in depletion of chromium in the grain boundary areas. This metallurgical structure is called "sensitized" structure.

In Type 430 stainless steel, a ferritic stainless steel containing 16 to 18% chromium, the basic mechanism of intergranular corrosion is the same as that of austenitic stainless steels. The sensitized microstructure is developed by chromium depleted zones near grain boundary. However, the sensitization heat treatment is quite different. For example, solution annealing of Type 430 stainless steel at temperatures above 1,000°C (1,832°F) followed by water quenching results in sensitized or lightly sensitiz-

ed microstructure in the alloy depending upon the sample size. On the other hand, the same heat treatment does not produce a sensitized microstructure in austenitic stainless steels. Diffusion rate of carbon and nitrogen in ferritic stainless steel is much faster than that in austenitic stainless steel. However, solubility of the interstitial elements in austenitic stainless steel is greater than that in ferritic stainless steel. During the solution annealing heat treatment the interstitial elements in both ferritic and austenitic stainless steels are in dissolved state. Subsequent water quenching is fast enough to prevent chromium carbide precipitates near the grain boundary in austenitic stainless steel. However, in Type 430 stainless steel the cooling rate during water quenching is not rapid enough to prevent the formation of these precipitates resulting in sensitization. Subsequent heating of Type 430 stainless steel at temperatures of 700-800°C (1,292-1,472°F) for 10 to 15 minutes heal the chromium depleted zone near the grain boundary by diffusion of chromium from inside of the grain. On the other hand, the same heat treatment results in a sensitized microstructure in austenitic stainless steel by forming chromium carbide precipitates near the grain boundary. Unlike austenitic stainless steels commercial grade Type 430 stainless steel contains chromium carbide precipitates after normal non-sensitization heat treatment.

Intergranular corrosion test methods can be classified as;

- 1) etching test,
- 2) immersion test, and
- 3) electrochemical test.

So far, most of the test methods in literature have been developed for measuring intergranular corrosion properties of austenitic stainless steels, primarily for 18 Cr-8 Ni type stainless steels. Due to the difference in corrosion

properties and metallurgical structures after normal non-sensitization heat treatment or welding, the test methods developed for 18 Cr-8 Ni type stainless steels cannot be utilized for determining intergranular corrosion properties of Type 430 stainless steel.

The ASTM committee A-1 has, therefore, established the standard practices for detecting susceptibility to intergranular attack in ferritic stainless steels (ASTM A763-79). This paper will outline recent development of intergranular corrosion test methods for Type 430 stainless steel. The test methods will include a new etching test, immersion tests, and an electrochemical potentiokinetic reactivation (EPR) test for Type 430 stainless steel.

## ETCHING TEST

The oxalic acid test (ASTM A262-A) has been the widely used etching test for determining intergranular corrosion properties of austenitic stainless steels after either heat treatment or welding. The test is simple and fast, however, this test cannot quantify the degree of sensitization (DOS) in the steels. This test consists of a 90 second electrolytic etching under an applied current density of 1 ampere/cm<sup>2</sup> in 10% oxalic acid solution. A step or dual structure after the etch test is acceptable, however, a ditch structure is not acceptable by the test. Application of this test to ferritic stainless steels has been limited due to dissolution of carbide precipitates in addition to chromium depleted regions in the steels by the test. Most commercial grades of ferritic stainless steels (except the extra low interstitial grades) may have a chromium carbide network along grain boundaries after normal, non-sensitizing heat treatments. When this chromium carbide network is developed in non-sensitized stainless steel, the test results will be incorrect due to dissolu-

tion of the carbide network forming ditch structure.

A chemical etch test has been developed to determine the susceptibility of Type 430 stainless steel to intergranular corrosion after either heat treatment or welding. Only chromium depleted zones are dissolved by the test. Details of the test procedures and results are discussed elsewhere<sup>(1,2)</sup>. Following is a brief description of the test procedures and results.

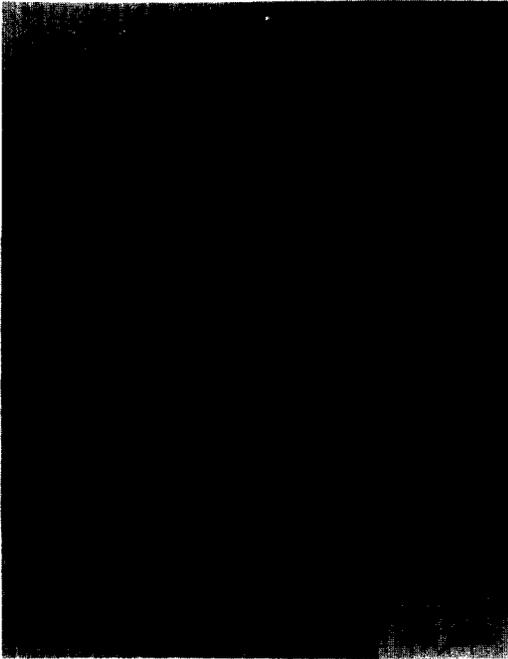
Samples are cut into specimens such that the total surface area exposed to the test solution is about 2 to 5 cm<sup>2</sup> (0.3 to 0.8 inch<sup>2</sup>). The surfaces of the specimens are polished to a 1 μm finish with a proper polishing device, rinsed with tap water, then degreased with acetone prior to final finishing with distilled water. The new etching test consists of a 5 minute etching in boiling 60% (by volume) sulfuric acid plus 120 g/l cupric sulfate (CuSO<sub>4</sub>·5H<sub>2</sub>O). A solution volume of 40 to 100ml is adequate for a test. Boiling chips should be added to prevent bumping of the test solution during a test. It is recommended to hold the specimen vertically during testing by employing a S-shaped glass hook in a hole drilled near one end of the specimen.

Figure 1 exhibits the test results for Type 430 stainless steel after the etch test. Figure 1. a is a test result of non-sensitized specimen [760°C (1,400°F), 1 hour, water quench]. The non-sensitized specimen does not exhibit any grain boundary attack after the etch test. The SEM micrograph of the specimen (Figure 2. a) exhibits a number of precipitates. The energy dispersive X-ray (EDX) analysis indicates that precipitate "A" in the figure contains a higher concentration of chromium than that of the alloy matrix, indicating that this precipitate is probably a chromium carbide particle. Precipitate "B" in Figure 2.a was identified as an

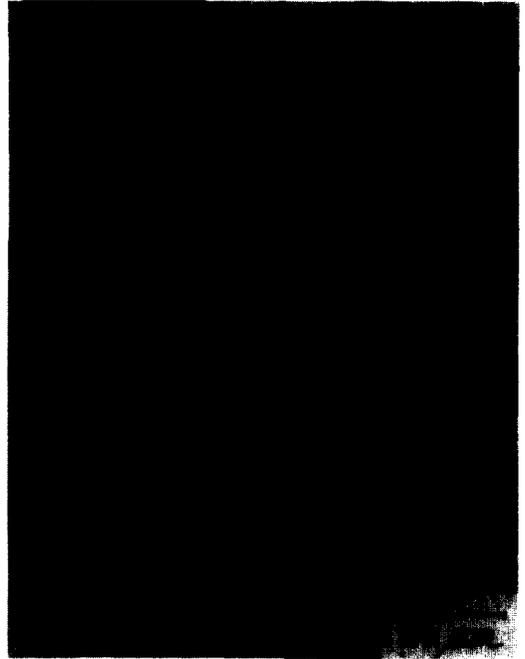
aluminum rich inclusion by the EDX analysis. The alloy subjected to sensitization heat treatment [1,093°C (2,000°F), 1 hour, air cool] exhibits distinct grain boundary "ditching" in the light micrograph (Figure 1.b). The SEM micrograph in Figure 2.b clearly reveals that the ditching is caused by grain boundary dissolution. The alloy subjected to heat treatment of 1,093°C (2,000°F) for an hour followed by water quench exhibited lightly sensitized microstructures. Partial grain boundary ditching (dual structure) is observed in Figure 1.c. The lightly shaded grains and bright grains in Figure 1.c indicate martensite and ferrite, respectively. Since the martensitic phase contains approximately 2 to 2.5% less chromium than the ferrite<sup>(3)</sup> and a highly strained crystal structure, it is less corrosion resistant. As a result, Figure 2.c clearly exhibits step structures between martensitic and ferritic grains after the etch test.

Figure 3 exhibits the etched structure of the alloy after the oxalic acid test. A dual structure was observed with the specimens of lightly sensitizing heat treatment [1,093°C (2,000°F), 1 hour, water quench]. Distinct ditching was exhibited with the specimens of sensitization heat treatment [1,093°C (2,000°F), 1 hour, air cool]. Unlike Type 304 austenitic stainless steel after the oxalic acid test, a flat structure resulting from general dissolution instead of a step structure was observed with the non-sensitized specimen [760°C (1,400°F), 1 hour, water quench]. SEM examination indicated that no carbides were detectable on the surface after the electrolytic etching in oxalic acid.

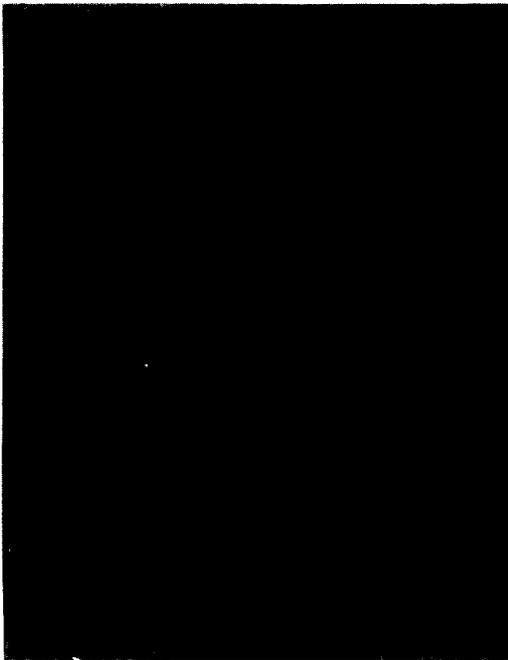
To investigate the stability of the chromium carbide precipitates after the new etch test, additional samples were prepared in such a way that the chromium carbides were extensively precipitated along grain boundaries without having the chromium depleted zones near the



a. Non-sensitized

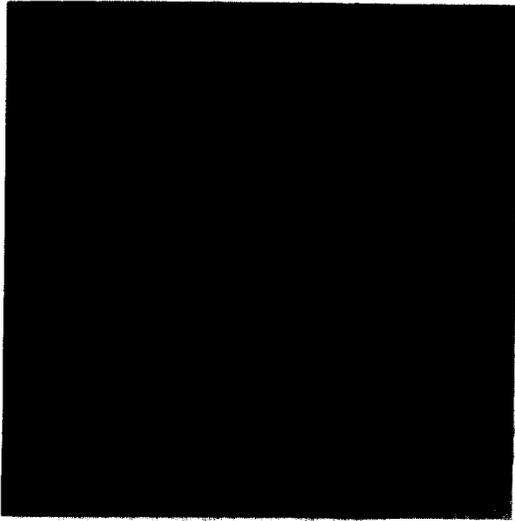


b. Sensitized

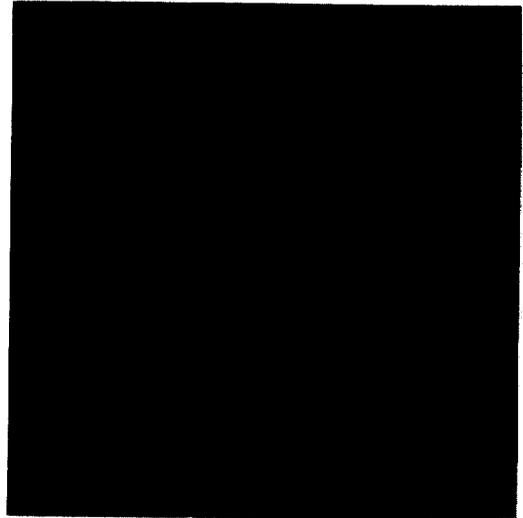


c. Lightly sensitized

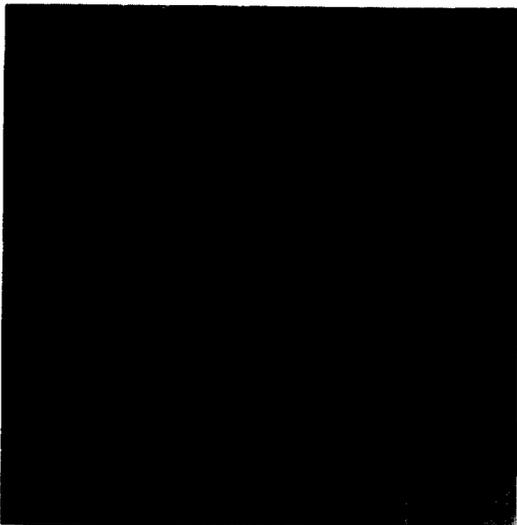
Fig. 1. Light Micrographs of Etched Structures Revealed in Type 430 Stainless Steel After the Etch Test in 60% Sulfuric Acid plus Copper Sulfate Solution (From Reference 1).



a. Non-sensitized

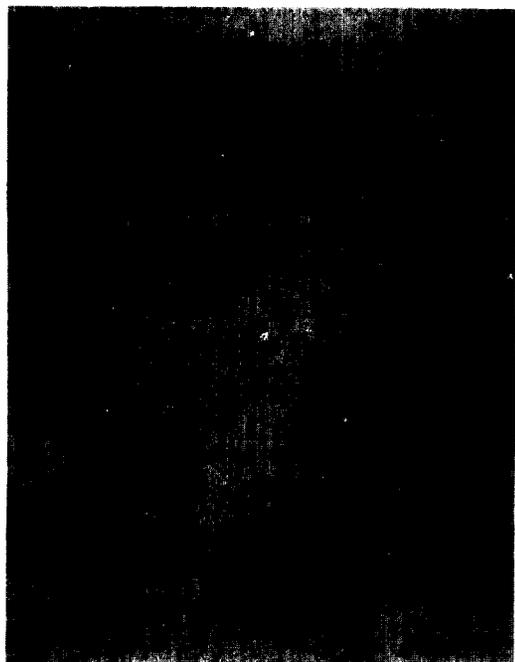


b. Sensitized



c. Lightly sensitized

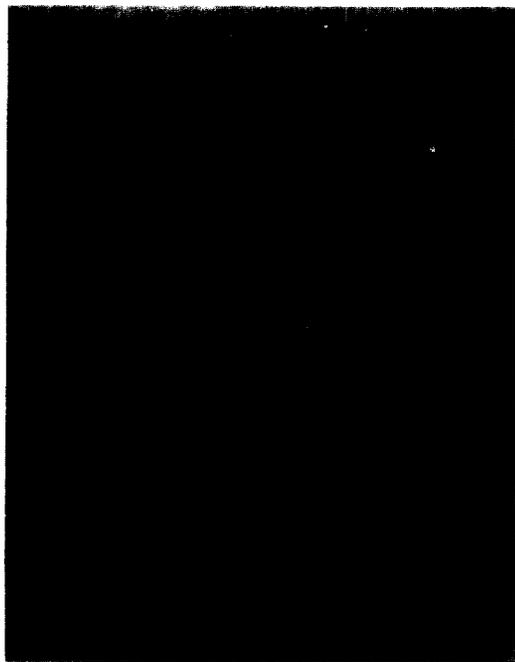
Fig. 2. SEM Micrographs of Etched Structures Revealed in Type 430 Stainless Steel After the Etch Test in 60% Sulfuric Acid plus Copper Sulfate Solution (From Reference 1).



a. Non-sensitized



b. Sensitized



c. Lightly sensitized

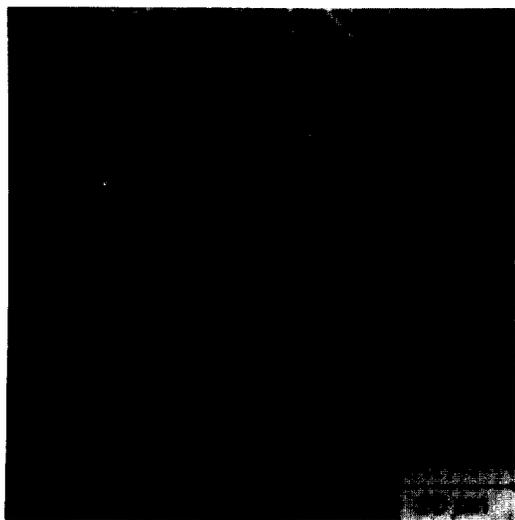
Fig. 3. Light Micrographs of Etched Structure Revealed in Type 430 Stainless Steel After the Oxalic Acid Etch Test (From Reference 1).

precipitates. This microstructure was developed by employing a heat treatment of  $760^{\circ}\text{C}$  ( $1,400^{\circ}\text{F}$ ) for 16 hours following the heat treatment of  $1,093^{\circ}\text{C}$  ( $2,000^{\circ}\text{F}$ ), 1 hour, air cool. The cupric sulfate immersion test results after 24 hour immersion confirmed that the specimen is non-sensitized. The test procedures of the cupric sulfate immersion test are described in the following section. The surface structure of these samples following the new etch test is compared with that after the oxalic acid test in Figure 4. The SEM micrographs in this figure clearly reveal that the new chemical etch test does not dissolve chromium carbide precipitates along grain boundaries, while the oxalic acid etch test attacks the carbides. Figure 4, therefore, indicates that the oxalic acid test may lead to misleading conclusions by dissolving chromium carbide precipitates along grain boundaries, in addition to dissolving chro-

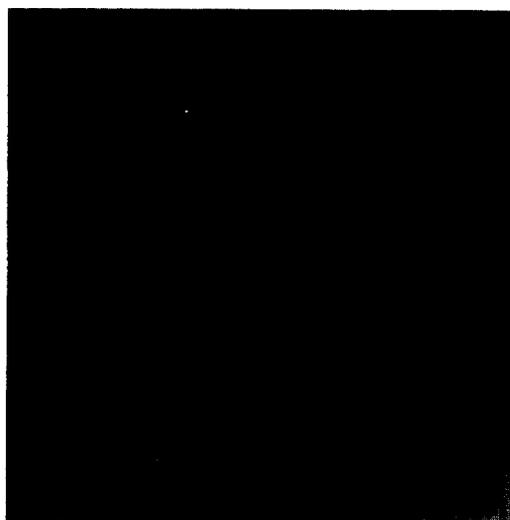
mium depleted regions. For example, the non-sensitized specimen shown in Figure 4 is not acceptable by the oxalic acid etch test criteria.

The above results indicate that the new chemical etch test should be used in place of the oxalic acid etch test for Type 430 stainless steel. The absence of grain boundary ditching after the new etch test indicates that a specimen is non-sensitized. The criteria for evaluating the susceptibility of the alloy to intergranular corrosion after the new etch test are the same as those used after the oxalic acid etch test.

The results of the new etch test are compared with those of other intergranular corrosion tests. Details of the test procedures of the intergranular corrosion tests listed in Table 1 are described in the succeeding sections. The DOS which was quantified by the immersion tests and the EPR test indicates that the DOS for specimens after heat treatment 3 [ $1,093^{\circ}\text{C}$



a. The New Chemical Etch Test



b. The Oxalic Acid Etch Test

Fig. 4. SEM Micrographs of Etched Structures Revealed in Type 430 Stainless Steel After the Heat Treatment of  $1,093^{\circ}\text{C}$  ( $2,000^{\circ}\text{F}$ ), 1 Hour, Air Cool, Followed by  $760^{\circ}\text{C}$  ( $1,400^{\circ}\text{F}$ ), 16 Hours, Water Quench (From Reference 2).

TABLE 1.  
INTERGRANULAR CORROSION TEST RESULTS OF TYPE 430 STAINLESS STEEL

Heat Treatment	Ferric Sulfate Immersion Test, mm/yr. (in./mo.)	Cupric Sulfate Immersion Test, mm/yr. (in./mo.)	EPR Test Pa; coul/cm <sup>2</sup>	Chemical Etch Test	Oxalic Acid Etch Test
1. 760°C (1,400°F), 1 hour, Water Quench (non-sensitizing)	3.75(0.0123)	2.10(0.0069)	0	flat	flat
2. 1,093°C (2,000°F), 1 hour, Air Cool (Sensitizing)	109.64(0.3597)	118.23(0.3879)	10.72	ditch	ditch
3. 1,093°C (2,000°F), 1 hour, Water Quench, (lightly sensitizing)	9.54(0.0313)	9.45(0.0310)	0.018	dual	dual

(2,000°F), 1 hour, WQ] was significantly lower than that for specimens after heat treatment 2 [1,093°C (2000°F), 1 hour, AC], and was only slightly worse than that for specimens after heat treatment 1 [760°C (1,400°F), 1 hour, WQ]. Results of the oxalic acid etch test and the new chemical etch test agree well with those of the immersion tests and the EPR test.

### IMMERSION TEST

The ferric sulfate (ASTM A262-B), the cupric sulfate (ASTM A262-E) and the nitric acid (ASTM A262-C) immersion tests have been widely used for determining intergranular corrosion properties of austenitic stainless steels, primarily the 18 Cr-8 Ni grades. The tests, except the cupric sulfate immersion test, can quantify the DOS in the steels, however, a drawback of the tests is lengthy testing time.

The ferric sulfate immersion test consists of a 120 hour immersion in 600 ml of a boiling

solution of 50% (by weight) sulfuric acid plus 25 g ferric sulfate ( $\text{Fe}_2(\text{SO}_4)_3 \cdot n\text{H}_2\text{O}$ ). The corrosion rate of specimens after the test expressed in the unit of mm per year (inch per month) is utilized as a measure of DOS. The cupric sulfate immersion test consists of a 24 hour immersion in 600 ml of a boiling solution of 16% (by weight) sulfuric acid plus 100g/liter copper sulfate ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ). After immersion the test specimens are bent through 180 degrees over a radius equal to the thickness of the specimens. Fissuring after bending indicates that the specimen is susceptible to intergranular corrosion, but this test cannot quantify the DOS. The nitric acid immersion test consists of exposure to boiling 65% nitric acid for five 48-hour periods. Sensitized material exhibits high corrosion rates in mm per year (inch per month). Because of the different corrosion properties of Type 430 stainless steel, specimens may dissolve completely during the

ferric sulfate or nitric acid immersion test period. The complete dissolution of test specimens during testing sometimes makes it difficult to quantify the DOS of samples. The ASTM A-1 committee recommends a 24-hour immersion in the ferric sulfate test solution for Type 430 stainless steel (ASTM A763-79).

This section will discuss the author's recent work on the modification of the ferric sulfate and cupric sulfate immersion test methods to quantify the DOS of Type 430 stainless steel<sup>(4)</sup>. For the study the specimen preparation procedures described in ASTM A-262 were followed. The following is a brief description of the test results.

#### A. Modification of the Ferric Sulfate Immersion Test (ASTM A262-B)

A sample of Type 430 stainless steel was heat treated to produce both sensitized [1,093°C (2,000°F), 1 hour, AC] and non-sensitized [760°C (1,400°F), 1 hour, WQ] specimens. Sulfuric acid concentrations of 25 to 50% (by weight) and ferric sulfate additions of from 25 to 80g were examined. Specimens were occasionally dissolved actively in the 600 ml sulfuric acid solutions containing 25 g ferric sulfate. To prevent this, 80 g of ferric sulfate was added to 600 ml of 25 to 40% sulfuric acid solutions. Only 40 g of ferric sulfate was added to 600 ml of 50% sulfuric acid solution since a greater amount would exceed the solubility limit of the boiling solution.

General corrosion of non-sensitized specimens increases as the acid concentration is increased. For a given length of exposure time, the ratio of intergranular to general corrosion (the ratio of the weight loss between sensitized and non-sensitized specimens) acts as a measure of the resolving power or sensitivity of the

solution to detect susceptibility to intergranular attack. The results in Figure 5 indicate that a 24-hour immersion test in a boiling 50% sulfuric acid plus 40 g ferric sulfate solution represents the optimum test condition for differentiating between sensitized and non-sensitized specimens (general corrosion rate/intergranular corrosion rate > 10). The corrosion rate of a sensitized specimen in 60% sulfuric acid solution is so rapid that the specimen is completely dissolved in several hours. Figure 6 exhibits the corroded surfaces of sensitized and non-sensitized specimens after the test. Only general corrosion is observed when the specimen is non-sensitized, while the sensitized specimen exhibits intergranular corrosion, resulting in undermining and dislodgment of grains. The sponge-like grains in the sensitized specimen (figure 6) are martensitic grains which contain about 2 to 2.5% less chromium than ferritic grains<sup>(3)</sup>. Most of the weight loss for the sensitized specimen was due to grain dropping, therefore, a specimen having larger grains exhibited a greater weight loss during the test. Generally, non-sensitized specimens of Type 430 stainless steel exhibit corrosion rates under 9mm/year (0.03 inch/month).

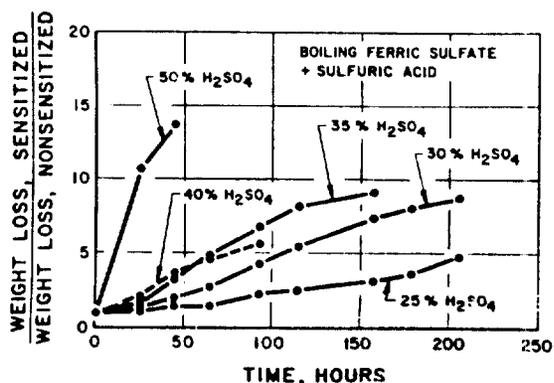
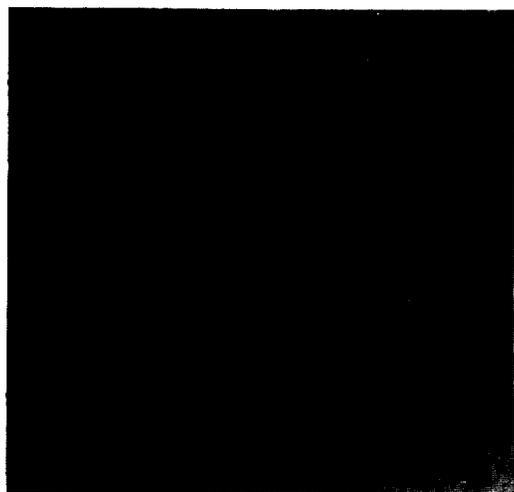
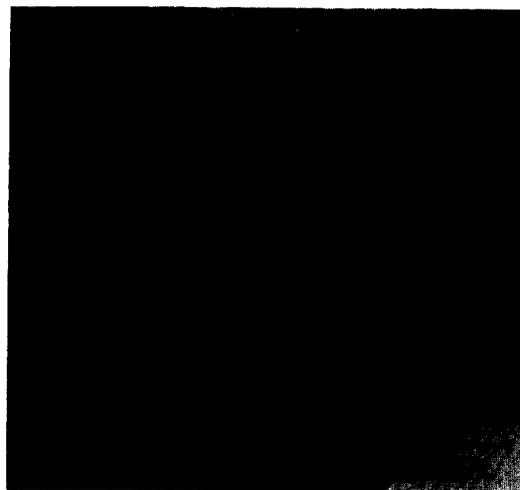


Fig. 5. Effect of Concentration of Sulfuric Acid on Corrosion of Type 430 Stainless Steel in Boiling Ferric Sulfate-Sulfuric Acid Solutions (From Reference 4).



a. Sensitized



b. Non-sensitized

Fig. 6. SEM Micrographs of the Corroded Surface of Type 430 Stainless Steel After the Modified Ferric Sulfate-50% Sulfuric Acid Test (From Reference 4).

This study confirms that the test method recommended in the ASTM A 763-79 is pertinent. However, 40 g of ferric sulfate instead of 25 g is suggested for the test. Sometimes 40 g of ferric sulfate is not dissolved readily in boiling 50% sulfuric acid solution. During the testing the undissolved portion of ferric sulfate dissolves as corrosion of the test specimen consumes ferric sulfate. The excess amount of ferric sulfate in the initial test solution did not affect the test results.

#### B. Modification of the Cupric Sulfate Immersion Test (ASTM A262-E)

Sensitized [1093°C (2,000°F), 1 hour, AC] and non-sensitized [760°C (1,400°F), 2 hour WQ] Type 430 specimens were tested in 600ml of boiling 30, 40, and 50% (by weight) sulfuric acid plus 72 g cupric sulfate ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ) solutions to determine the optimum test condition for detecting intergranular corrosion attack

of the alloy. A piece of copper metal about 3mm x 20mm x 37.5mm (0.1in. x 0.8in. x 1.5in.) with a bright, clean finish was placed in the flask on a glass cradle avoiding contact of the copper plate with the test specimen. Allihn condensers having a 25mm (1 inch) long drip tip were employed. It has been reported that the length of the Allihn condenser drip tip has an effect on the corrosion rate of specimens subjected to the cupric sulfate immersion test.<sup>(5,6)</sup> The results in Figure 7 indicate that any of the three test solutions can be utilized for the test, but a longer test period is required with a lower concentration of sulfuric acid. The optimum test condition is, therefore, a 24-hour immersion in 600ml of boiling 50% sulfuric acid plus 72g cupric sulfate solution. Sensitized specimens corroded rapidly in 60% sulfuric acid solution, therefore this solution is not suitable for the immersion test.

The corroded surfaces of the sensitized

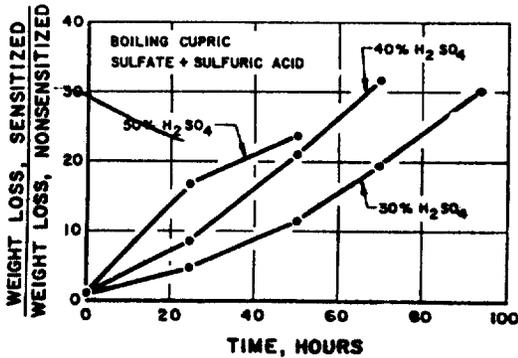


Fig. 7. Effect of Concentration of Sulfuric Acid on Corrosion of type 430 Stainless Steel in Boiling Copper-Copper Sulfate-Sulfuric Acid Solutions (From Reference 4).

and non-sensitized specimens after the 24-hour test in 600ml of boiling 50% sulfuric acid plus 72g cupric sulfate solution are identical to those observed after testing in the boiling 50% sulfuric acid plus ferric sulfate solution (Figure 6). Metallic copper deposit was often found on the surface of test coupons of samples exhibiting a high weight loss. The copper deposit on the specimens may hinder further corrosion during testing, but this should not be a major problem for the test. No copper was deposited on non-sensitized specimens. This copper deposit should be removed carefully before weighing the specimen. The results of the modified cupric sulfate immersion tests are compared with those of other intergranular corrosion tests including the modified ferric sulfate immersion test for Type 430 in Table 1 and good agreement is observed. Slightly lower corrosion rates are exhibited with the modified cupric sulfate immersion test, but both of the tests are capable of quantifying the DOS of Type 430 stainless steel after various heat treatments. Initial tests on specimens water quenched after a solution anneal at 1093°C (2,000°F) did not produce consistent results as a result of variation in cooling rate and lack of experimental control.

The actual cooling rate of a large sample is slower during water quenching than that of a small sample and, therefore, exhibits greater DOS. For the present study samples 1.3mm x 25mm x 150mm (0.05in. x 1in. x 6in.) were heat treated.

## ELECTROCHEMICAL TEST

The utilization of electrochemical techniques for quantifying the DOS of austenitic stainless steels has been actively studied for the last 10 years. The electrochemical tests have the following advantages over the conventional immersion test methods described by ASTM A 262:

1. It is fast; the electrochemical tests are generally completed within 30 minutes. The ASTM standard immersion tests require 24 to 240 hours for a test.
2. The DOS of lightly sensitized stainless steels can be quantified; the lightly sensitized steels which may not be detected by the ASTM immersion test methods have potential problems of intergranular stress corrosion cracking in a certain corrosive environments.
3. It can be non-destructive; the ASTM tests require cutting of the test samples.

However, the electrochemical test methods require additional instrument, such as a potentiostatic unit and a coulometer, and complicated test procedures. Therefore, only a well trained technical person should conduct the tests.

The principle of electrochemical potentiokinetic reactivation (EPR) method, an electrochemical technique, was first suggested by P. Novak et. al.<sup>(7)</sup> and V. Cihal et. al.<sup>(8)</sup> and was later adopted by W.L. Clarke et. al.<sup>(9)</sup> The test, as applied to Type 304 stainless steel, consists of reactivating a specimen by changing the potential at a rate of 100mV/minute toward

the open circuit potential following passivation of the specimen at  $+200\text{mV}_{\text{SCE}}$  for 2 minutes. The test solution is deaerated 1 N sulfuric acid + 0.01 N potassium thiocyanate at  $30^\circ\text{C}$  ( $86^\circ\text{F}$ ). Potassium thiocyanate is a grain boundary activator, therefore, it enhances grain boundary attack during the reactivation step when the specimen is sensitized. Non-sensitized stainless steels exhibit a low current density during the reactivation step due to the stability of the film formed during passivation (Figure 8).

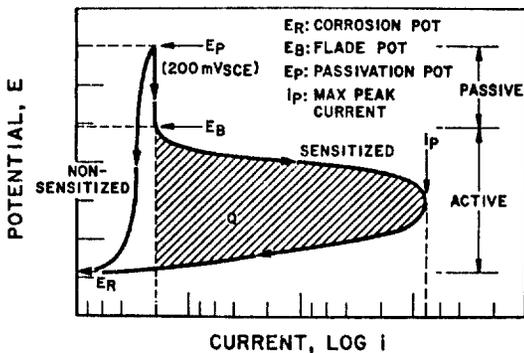


Fig. 8. Schematic Curve of EPR Test.

The criteria used to distinguish between non-sensitized and sensitized specimens include the activation charge,  $Q$  (given by the integrated area below the reactivation peak of the curve), the peak current density,  $i_p$ , in the active state, and the potential,  $E_B$  (Flade potential), at which the active curve breaks upward. The value  $Q$  is further normalized according to total grain boundary area to permit direct comparison of different materials which may exhibit different  $Q$  values solely as a result of grain size differences ( $P_a = \text{normalized } Q$ ). V. Cihal, et al. utilized this test with 5 N sulfuric acid at  $70^\circ\text{C}$  ( $158^\circ\text{F}$ ) for studying the sensitization of Type 304 stainless steel<sup>(8)</sup>. The principle of the test is the same as that of the EPR test with 1 N sulfuric acid + 0.01 N potassium thiocyanate solution. The same EPR test methods, however,

cannot be employed for Type 430 due to the difference in corrosion properties<sup>(10)</sup>.

Another electrochemical technique which is basically a potentiokinetic anodic polarization test utilizing a 1 N perchloric acid + 0.2 N sodium chloride solution at room temperature was suggested by L. A. Medvedeva, et al.<sup>(11)</sup>. P. Chung and S. Smialowska adopted this test for studying the intergranular corrosion of Type 304 stainless steel<sup>(12)</sup>. The current density of the secondary active peak in the polarization curve is the criterion for the DOS of specimens. Sensitized specimens exhibit a large secondary active peak, while non-sensitized ones do not show this peak. This test was evaluated by the author for a possible utilization of the test for Type 430<sup>(10)</sup>. However, the results indicated that a lightly sensitized specimen cannot be differentiated from a non-sensitized one by the test.

The author has recently proposed an EPR test method for determining intergranular corrosion properties of Type 430 stainless steel.<sup>(10, 13)</sup> A brief description of the test is as follows. A 3 N  $\text{H}_2\text{SO}_4$  solution at  $30^\circ\text{C}$  ( $86^\circ\text{F}$ ) is utilized for the test. The test consists of passivating a specimen at  $+400\text{ mV}_{\text{SCE}}$  for 10 minutes, followed by reactivating the specimen by decreasing the potential at a rate of  $250\text{mV}/\text{minute}$  toward the open circuit potential.

The above procedure was determined from the following data. A polarization curve for a sensitized Type 430 stainless steel in a 5 N  $\text{H}_2\text{SO}_4$  solution indicates that a stable passive film forms near  $+400\text{ mV}_{\text{SCE}}$ . When the passivation time is shorter than five minutes, non-sensitized Type 430 stainless steel with a chromium content near 16% exhibits a small active peak (peak current density of  $0.3\text{mA}/\text{cm}^2$ ), which is not a result of grain boundary dissolution. When the chromium content of the alloy

is 17 or 18%, the five-minute passivation time was sufficient. The small active peak for the alloy of 16% chromium disappeared when the passivation time was increased to 10 minutes.

Figure 9 illustrates the test results for Type 430 as a function of heat treatment. Absence of the active peak during the reactivation step of the EPR test indicates the specimen is non-sensitized. Light micrographs of the exposed sample surface after testing (Figure 10) show grain boundary attack when the specimens are sensitized. The results in Table 1 indicate that both the immersion and the EPR tests can detect the lightly sensitized samples. The results of the immersion and the EPR tests in Table 1 agree qualitatively well with each other. However there is a lack of quantitative agreement between the tests. Ratio of a sensitized sample to a lightly sensitized sample is 11.5 by the ferric sulfate immersion test and 12.5 by the cupric sulfate immersion test. This compares to a ratio of 596 by the EPR test.

In immersion test, the corrosion rates are primarily due to weight loss from grain droppings. This is caused by grain boundary dissolution. Therefore, the larger the grain size the greater the weight loss, even with the same DOS. In the EPR results the DOS is measured

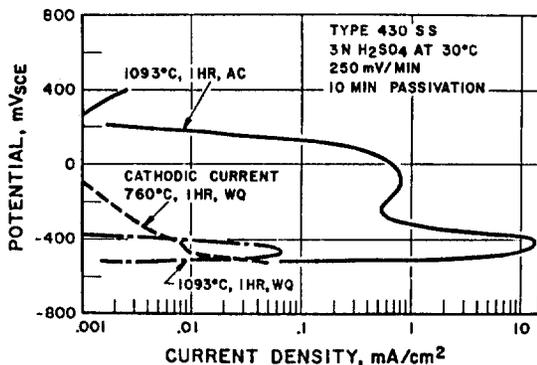


Fig. 9. The EPR Test Results of Type 430 Stainless Steel (From Reference 13).

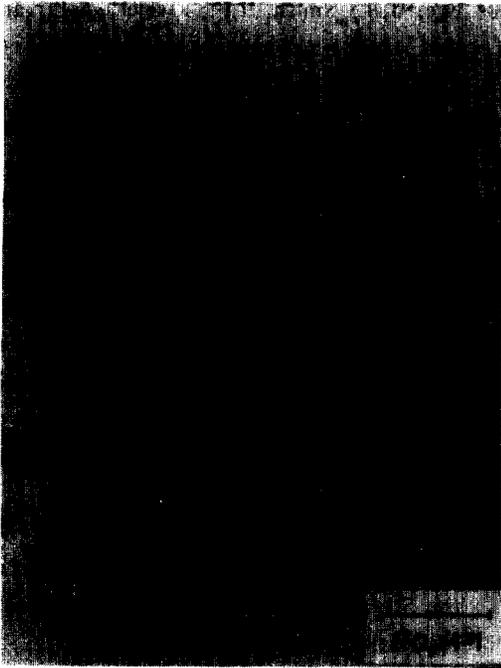
by dissolution of grain boundary and the values are normalized with respect to grain size. No direct comparison can be made from the results of immersion tests and EPR tests. Acceptance limit of the test results should be determined on the basis of the test method employed and the individual corrosive environment when the material is actually used.

Mill bright annealed specimens of Type 430 often show an active peak of about 0.2mA/cm<sup>2</sup> during the EPR test. This is not a result of grain boundary dissolution. A similar active peak is also observed with other grades of mill bright annealed stainless steels. This test, therefore, should not be utilized for quantifying the DOS of samples subjected to a mill bright annealing treatment. An additional non-sensitization heat treatment after mill bright annealing eliminates the appearance of the small active peak. Since the bright annealing treatment is normally conducted in an atmosphere of dissociated ammonia gas (75% H<sub>2</sub>, 25% N<sub>2</sub>), nitrogen may diffuse into the metal, forming chromium nitrides, thus lowering the effective chromium content in the alloy matrix near the surface. No definitive explanation can be given in this paper, however, for the appearance of an active peak during the reactivation step with mill bright annealed specimens.

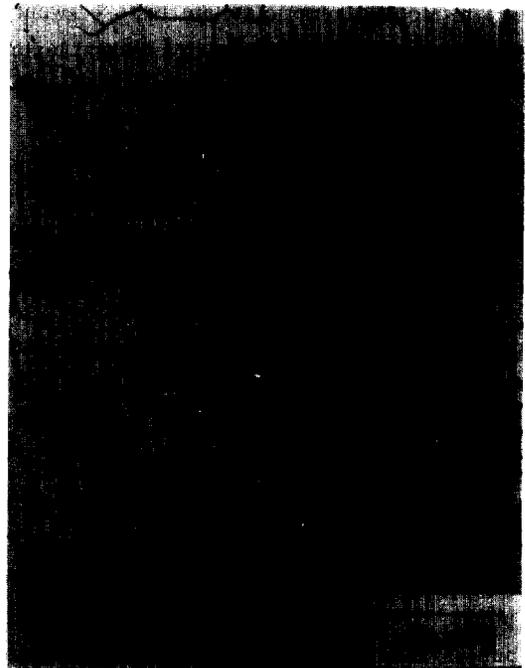
## CONCUSSIONS:

Intergranular corrosion testing methods for Type 430 stainless steel were described. These are;

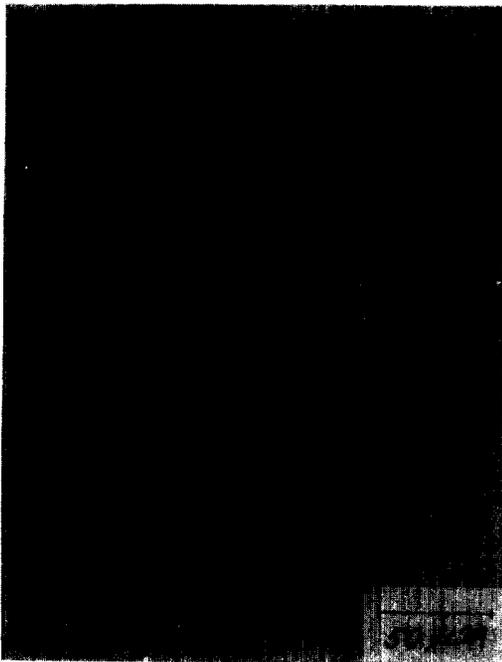
1. Etching test: Five minute etching in boiling 60% (by volume) sulfuric acid plus 120 g/l cupric sulfate.
2. Immersion test:
  - a. Modified ferric sulfate test - Twenty-four hour immersion in a 600 ml boiling 50% (by weight) sulfuric acid plus 40 g ferric sulfate solution.



a. Non-sensitized



b. Sensitized



c. Lightly sensitized

Fig. 10. Microstructures Revealed in the Specimens of Type 430 Stainless Steel After the IPR Test in 3N Sulfuric Acid (From Reference 13).

b. Modified cupric sulfate test – Twenty-four hour immersion in a 600 ml boiling 50% (by weight) sulfuric acid plus 76 g cupric sulfate solution.

3. EPR test: Passivation of a specimen at +400 mV<sub>SCE</sub> for 10 minutes, followed by reactivating the specimen by decreasing the potential at a rate of 250mV/minute toward the open circuit potential.

The tests can be utilized for determining intergranular corrosion properties of both heat treated and welded Type 430 stainless steel.

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