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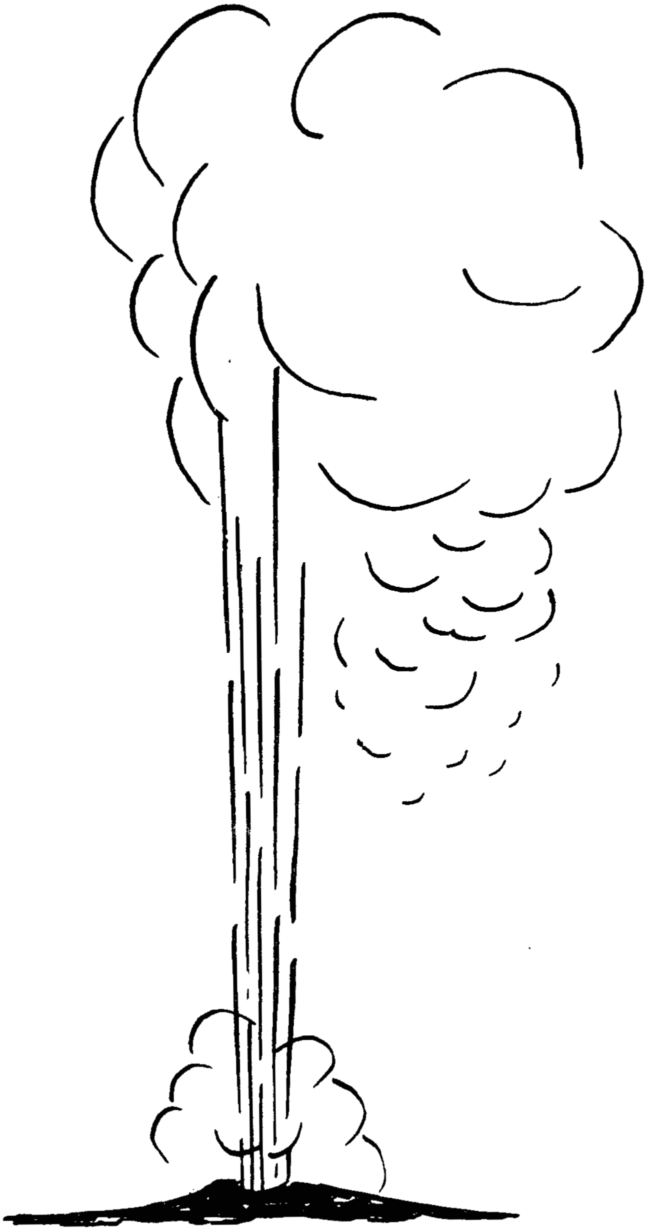

ADDENDUM TO MATERIAL SELECTION GUIDELINES FOR GEOTHERMAL ENERGY UTILIZATION SYSTEMS

Part I: Extension of the Field Experience Data Base
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RESISTANCE OF NITROGEN-CONTAINING STAINLESS ALLOYS TO CORROSION IN CHLORIDE MEDIA

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ABSTRACT

The pitting resistance of a series of experimental stainless steels with varying amounts of nickel, chromium, molybdenum, manganese and nitrogen and a number of commercial stainless steels and nickel based alloys has been studied in highly concentrated chloride media. The results show that nitrogen enhances the pitting resistance of stainless steel and exceptional corrosion resistance is achieved with high levels of nitrogen in combination with suitable amounts of molybdenum and chromium.

INTRODUCTION

Effects of alloying elements on pitting resistance of stainless steel have been studied by many investigators(1-19). There is general acceptance of the beneficial effects of Cr and Mo additions. Beneficial effects of nitrogen were reported for stainless steel with and without added Mo and Si. The literature also covers other combinations of Mo and N, but only where relatively low contents of one are combined with higher contents of the other. It is for this reason that the present work emphasized alloys where both additions are on the high side.

During the course of our work, we found at least one combination that showed pitting resistance comparable to that of Hastelloy alloy C276 at a much lower cost, i.e., with about 20% Ni, 24% Cr, 6% Mo and added nitrogen, balance Fe.

EXPERIMENTAL PROCEDURE

The stainless steels evaluated in this study were prepared in small amounts from commercially pure grades of Fe, Ni, ferrochrome, Mn, Mo, Si, manganese or chromium nitride, and chromium carbide. Melting was done in a vacuum induction furnace. The melting procedure consisted of (1) melting Fe, Ni, Mo, Mn and ferrochrome in a vacuum, (2) bleeding nitrogen into the furnace, and (3) introducing Mn_4N or CrN, wrapped in iron foil, into the melt. Ingots were soaked for 30 minutes and hot-rolled. The temperatures were 1205°C and 1095°C, depending upon hot ductility of the heats. The hot-rolled specimens were pickled in a solution containing 10% NHO_3 and 2% HF at 65°C to remove the hot working scale, cold-rolled to 2 mm, annealed at 1065°C for 5 minutes, water quenched, and pickled again. Table 1 shows the compositions of 5 experimental heats that were most resistant out of a group of 30.

We conducted the following tests on the experimental alloys and commercially produced controls. The specimens were flat coupons that were ground, polished to 600 grit, rinsed in distilled water, degreased and dried.

a) Ferric Chloride Test

The immersion test was done for six days at 30°C in 6 w/o $FeCl_3$. Specimens that showed very slight weight loss were put into the solution again.

b) Polarization Test

Strips of 1.25 cm x 1.25 cm were subjected to anodic polarization in deaerated 1N NaCl solution at 30°C. The specimens were mounted in epoxy, and masked with lacquer, exposing approximately 1 cm^2. Testing was done in a one liter polarization cell, after deoxygenating the solution with prepurified nitrogen. Polarization started 50 minutes after the immersion at a scanning rate of 20 mV/min. All potentials were measured versus a saturated calomel electrode.

The experimental alloys that exhibited good corrosion resistance were tested by anodic polarization in more aggressive environments containing higher chloride ion concenration, at higher temperature and lower pH. These tests were conducted using a scan rate of 6 mV/min.

c) Crevice Test

The corrosion resistance of the experimental alloy showing the most promising results in the above tests was further compared with that of the highly corrosion resistant nickel base alloys Hastelloy alloys G and C-276, in a crevice corrosion test in ferric chloride. Crevices were induced by using TFE-fluorocarbon blocks and rubber bands, according to ASTM standard procedures. The tests were at 50°C for 96 hours, and the $FeCl_3$ was 6 w/o.

d) Copper Chloride - Ferric Chloride - Acid Test

A solution of 7(vol)% H_2SO_4 + 3(vol)% HCl + 1 wt.% $FeCl_3$ + 1 wt.% $CuCl_2$ was made from reagent grade materials. The temperature was boiling and the duration was 24 hours.

RESULTS AND DISCUSSION

a) Preliminary Immersion and Polarization Tests

Results for the resistant alloys of interest and commercial alloys are shown in Table 2. The weight loss of some specimens (not shown) in ferric chloride varied widely. Several of the experimental and commercial alloys did not suffer any measurable weight loss. Most of the alloys exhibited active-passive behavior during anodic polarization. The critical pitting potential in Table 2 (E_C) indicates breakdown of passivity and propagation of actively growing pits. A metal with a more noble value is more resistant to localized corrosion compared to a metal with a less noble E_C in the same environment.

Weight loss data in the ferric chloride solution correlated well with the anodic polarization data in sodium chloride solution in that alloys with small weight loss values were generally accompanied by more noble E_C values. There were, however, a few exceptions. Some of the experimental alloys with a relatively large amount of manganese showed no weight loss in ferric chloride, but broke down during anodic polarization.

Alloys 26 through 30, which contain the higher amounts of molybdenum and nitrogen and little manganese, suffered no weight loss or breakdown of passivity. These 5 alloys were selected for more rigorous testing.

b) Polarization Tests in More Aggressive Environments

Tests in more aggressive environments gave a better separation of corrosion resistance, as is evident from the E_C values in Table 2 for selected alloys in deaerated 1N NaCl + 0.5N HCl at 50°C (pH 0.69). As expected, these were generally smaller than in 1N NaCl, except for the alloys which did not break down in either of the two environments, such as the nickel- and titanium-based alloys and four of the high nitrogen bearing experimental alloys, i.e., Alloys No. 26, 28, 29 and 30. Nitrogen causes a significant improvement in the corrosion resistance, whereas manganese appears not to impart any significant corrosion resistance to stainless steels in the chloride environments.

Alloy No. 30 was chosen for more detailed investigation because of the lower cost (less nickel) compared to Alloy 28.

Figure 1 shows the anodic polarization curves for Alloy No. 30, alloys C-276 and G in deaerated 1N NaCl + 0.5N HCl at 70°C. The polarization curve for stainless steel Type 316 is also included in the figure for comparison. Alloy No. 30 and alloy C-276 did not suffer any breakdown in this solution, whereas alloy G exhibited a small range of passivity up to about 0.2V followed by a rapid increase in current density. The anodic scan was reversed in all cases. The pronounced hysteresis in the polarization curve of alloy G indicates its relatively poor resistance to localized corrosion. At the end of the test, the specimen surfaces were examined under a microscope and pits were visible in 316 stainless steel and alloy G. Also, very active protection potentials, E_p, were found for these 2 alloys i.e., the potential at which the forward and reverse scans intersect, implying that active pits in 316 stainless steel and alloy G would possibly continue to grow in this environment with little prospect for repassivation. Stainless steel 316 lacks any clear passive region. Neither alloy C-276 nor Alloy No. 30 displayed any hysteresis; the rapid increase in current density for these alloys around 0.9V is due to electrolysis of water, without any pitting.

Figure 1 also shows that Alloy No. 30 had a somewhat smaller passive current density than alloy C-276 in this environment. Table 3 shows the $i_{passive}$ values for alloys C-276, G and Alloy No. 30 at three different temperatures in deaerated 1N NaCl + 0.5N HCl, +0.2V. Values in all three alloys increased with temperature; the rise was very steep for alloy G and relatively slow for the other two alloys. However, Alloy No. 30 displayed lower currents than alloy C-276 at all three temperatures.

The anodic polarization curves for alloys C-276 and G and Alloy No. 30 in deaerated 2N NaCl + 0.5N HCl at 70°C are illustrated in Figure 2. The polarization curve for alloy G does not show any distinct passive region and it is poorly resistant. Alloy C-276 and Alloy No. 30 did not break down in this highly aggressive environment.

c) Crevice Corrosion Test

Crevice corrosion tests in ferric chloride solution at 50°C for stainless steel Type 316, alloy G, alloy C-276 and Alloy No. 30, showed that Type 316 stainless steel almost disintegrated, and alloy G suffered significant crevice corrosion underneath the TFE-fluorocarbon block, while alloy C-276 and Alloy No. 30 appeared to be immune to crevice corrosion. This test confirms the results of polarization tests.

Alloy No. 30 (Table 1) has roughly 2.5% more chromium and 0.4% less molybdenum than alloy G. However, Alloy No. 30 has 0.44% nitrogen which seems to be responsible for its much superior corrosion performance compared to alloy G. Although Alloy No. 30 has about 8% more chromium than alloy C-276, it has approximately 10% less molybdenum and much less nickel, so that it will be relatively cheap. The higher chromium content probably gives the lower passive current density for Alloy No. 30 compared to alloy C-276, but the unexpectedly low sensitivity to pitting appears due to nitrogen.

d) Immersion Test in 7 vol.% H_2SO_4 + 3 vol.% HCl + 1 Wt.% $FeCl_3$ + 1 Wt.% $CuCl_2$

Alloy No. 30 and alloy C-276 suffered some surface deterioration accompanied by small pits as shown in Figures 3(a,b) respectively. Alloy 30, however, suffered a much lower weight loss (1.8 mdd) than alloy C-276 (78.1 mdd). A repeat test in the above solution but with about half the original strength of HCl gave essentially similar results.

e) Microstructure: The experimental alloys with relatively large amounts of nickel, nitrogen and manganese were all fully austenitic; some of the low nickel ones contained ferrite when examined by a Magnegage. The microstructure of high nitrogen bearing Alloy 30 is shown in Figure 4. It is evident that Alloy No. 30 has some inclusions. The surface of the polished but unetched specimen when examined under the microscope revealed about an equal distribution and size of inclusions as in the etched micrograph. Etchants such as electrolytic oxalic acid or eletrolytic chromic oxide gave essentially similar structure and inclusion distribution. The matrix and the inclusions were analyzed by Energy dispersive x-rays (EDAX) and the resulting spectra show that the inclusions have more Mo and Cr and less Fe than the matrix.

f) Role of Nitrogen: The role of nitrogen in enhancing the corrosion resistance is not clear, and may be asociated with many details regarding the reactions between the surface electrolyte and the metal, as well as inclusions in the metal surface. One aspect is that nitrate ions are known to inhibit the anodic dissolution processes in many environments. Therefore, further tests were conducted with and without 0.1N $NaNO_3$. The results for AL-6X and Sandvik SAF 2205 clearly showed that $NaNO_3$ substantially improves the pitting resistance of both alloys in this environment, evidently due to the beneficial effect of NO_3^- ions. However, whether nitrogen atoms play any specific role in this process is a matter of speculation. When one compares the polarization behavior of Alloy No. 30 (Figure 1) and AL-6X (not shown) in 1N NaCl + 0.5N HCl, the effect of dissolved nitrogen in the metal becomes obvious. Alloy No. 30 has about 4% more Cr and 4% less Ni than AL-6X alloy. However, the markedly superior corrosion resistance of Alloy No. 30 with 0.44N to that of AL-6X alloy with only 0.018N may be ascribed primarily to the extra nitrogen, as was done earlier when Alloy No. 30 was compared to alloy G. Truman et al.(20) recently studied the effect of nitrogen addition on pitting corrosion of a series of austenitic stainless steels and observed that when the Cr and Mo contents were sufficiently high, a large increase in pitting resistance resulted from a small increase in nitrogen, apparently due to synergistic effects. The maximum Mo content of the alloys that they investigated was 3% and the effect of nitrogen was especially evident in a steel with 22% Cr, 3% Mo, 20% Ni and 0.455N. However, our results show that still further enhancement of pitting resistance can be achieved by increasing the Mo content to, for example, about 6%. At this level, corrosion resistance similar to alloy C-276 can evidently be achieved, as in the case of Alloy No. 30. It is further believed that N additions can, and do, increase the localized corrosion resistance of an entire range of Fe-Cr-Ni-Mo alloys.

g) Linear Regression

A multiple linear regression analysis was done, using pitting potential data from commercial alloys with and without N, as well as some of the less resistant experimental alloys. This computer analysis showed highest positive coefficients for N and Mo, and less so for Cr. Extrapolations were then made (computer) for several commercial alloys at the low and high end of resistance as well as for alloy #30. Results showed quite reasonable predictions except for the high N alloy (#30) which was predicted to pit even in the less aggressive solutions. Since no pitting occurred even in the most aggressive, hot environments, it is believed that the present observations for these alloy types are unique.

h) Practical Aspects

There is an obvious economic advantage in using nitrogen in stainless steel. Nitrogen can be substituted in part for more expensive argon during refining and the austenite forming tendency of nitrogen can be used to replace some of the more expensive austenite stabilizers such as nickel.

The present alloy development program was initiated in response to the need for more corrosion resistant alloys for use in the geothermal industry. However, because of its significant corrosion resistance, the nitrogen bearing stainless steel has has the potential of wider application in many other industrial areas.

CONCLUSIONS

1. The corrosion resistance of austenitic Fe-Cr-Ni-Mo stainless steels in chloride and acid chloride media can be significantly improved by addition of nitrogen. One high nitrogen bearing (0.44 N) alloy offers corrosion resistance comparable to that of Hastelloy alloy C-276, but at much reduced Ni and Mo levels.

2. Since nitrogen can replace some of the nickel in the alloy and part of the argon used during manufacturing of the alloy, considerable cost saving is possible by using nitrogen as a constituent of the alloy.

3. Manganese does not seem to significantly improve the corrosion resistance of stainless steel in the environment under investigation.

4. Further work is needed to manufacture larger heats of some of the nitrogen bearing alloys and test them in order to assess their commercial viability.

5. Linear regression analysis does not predict the unexpectedly large increase in pitting resistance that was observed in our high nitrogen alloy.

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TABLE 1

Composition of 5 of the Experimental Heats and Some Commercial Alloys

Alloy	N	Mo	C	Ni	Si	Cr	Mn	Other
26	0.339	5.84	0.010	25.09	0.25	17.35	--	--
27	0.390	6.11	0.011	25.90	0.29	18.35	--	--
28	0.422	5.94	0.011	25.36	0.30	24.75	--	--
29	0.442	5.87	0.014	19.09	0.26	20.14	--	--
30	0.440	6.06	0.018	19.90	0.30	24.32	--	--
SS 316	--	2-3	<0.08	10-14	--	16-18	--	--
Alloy C-276	--	15.80	0.003	Balance	--	15.61	--	0.19V, 1.4 Co, 3.6 W
Alloy G	--	6.42	0.014	Balance	--	21.89	--	2.24 (Cb + Ta), 1.78 Cu, 2.29 Co, 0.65 W
AL-6X	--	6.45	0.018	24.64	0.41	20.35	1.39	--
Sandvik Alloy SAF 2205	0.14	3.0	<0.03	5.5	--	22.0	--	--

Note: -- indicates none added.

TABLE 2

Corrosion Performance of Selected Alloys

Specimen	E_C (mV) 0.5 N HCl + 1N NaCl, 50°C	30°C $FeCl_3$ (mm/y)	E_C (mV) 1N NaCl, 30°C
26	-	0	-
27	281	0	-
28	-	0	-
29	-	0	-
30	-	0	-
Ti	-	0	-
Alloy 20 CB-3	-62	2.63	327
Alloy 625	-	0	-
Ti Code 12	-	0	-
Type 316	Not tested	0	-
Type 304	Not tested	8.7	108
AL 6X	195	0	562
Alloy C-276	-	0	-
Alloy G	-	0	-
Alloy S	-	0	-
SAF 205	-184	0	254
3RE 60	Not tested	3.0	231

(-) No breakdown in scanning to 908 mV.

TABLE 3

Passive Current Density for Alloys C-276 and G and Alloy No. 30 in Deaerated 1N NaCl + 0.5N HCl (pH 0.69)

$i_{passive}$ (A/cm^2) (at +0.2V SCE)	Temperature 25°C	70°C	90°C
Alloy C-276	6	25	70
Alloy No. 30	1.5	7.5	15
Alloy G	10	1,000	5,000

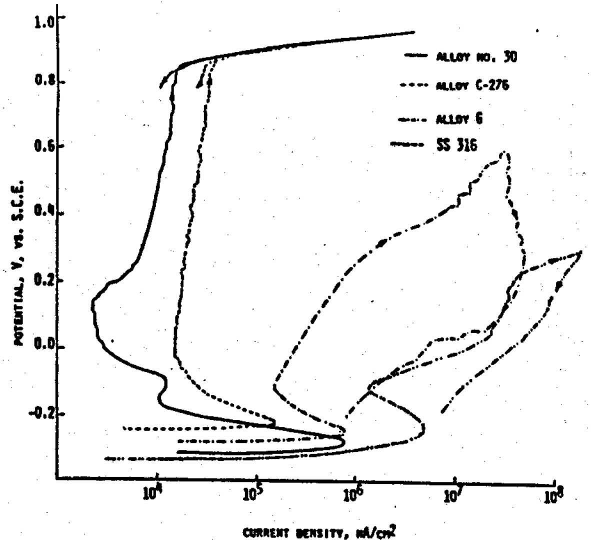

Fig. 1 Polarization Curves in 0.5N HCl + 1N NaCl at 70°C

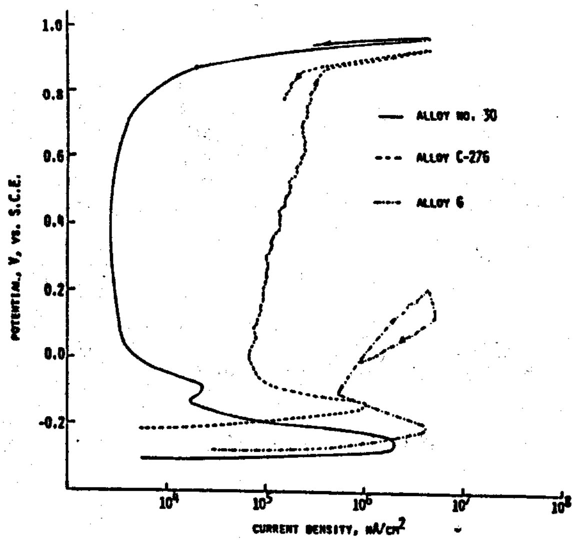

Fig. 2 Polarization Curves in 0.5N HCl + 2N NaCl at 70°C

200X

Fig. 3a Alloy #30 in H_2SO_4-HCl-$FeCl_3$-$CuCl_2$

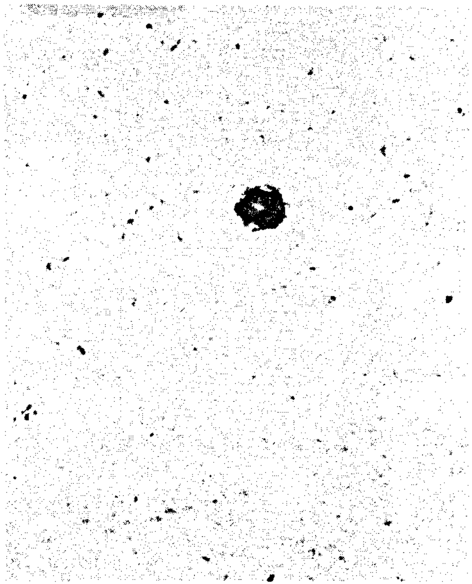

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Fig. 3b Alloy C-276 in H_2SO_4-HCl-$FeCl_3$-$CuCl_2$

400X 10% oxalic acid

Fig. 4 Structure of Alloy #30