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Assessment of Corrosion Behavior of Ductile Irons by Factorial Experiments

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The corrosion behavior of unalloyed and alloyed ductile irons (as cast, annealed, and cold worked) in sea water, dilute sulfuric acid, and dilute sodium hydroxide solutions was assessed. Specimen history had a significant effect on the corrosion potential except in ductile iron alloyed with Ni. When the specimens were subjected to different levels of cold working, the corrosion rate was influenced by both the history and the medium. Temperature had a significant effect on the corrosion rate except in the case of unalloyed ductile iron. Factorial experiments indicated that the cold-worked samples were more sensitive to the effect of temperature and composition on the corrosion rate as compared to annealed and as-cast samples. The medium had a significant effect on the corrosion rate in all the cases.

Keywords A: ductile iron, C: casting, E: corrosion

1. Introduction

Ductile iron (DI) is being used as an engineering material for more than five decades. In recent years, the production of DI castings in many countries has exceeded that of malleable iron castings and steel forgings. DI has better castability than steel and its mechanical properties can be tailor-made to the needs (Ref 1). There are soft ferritic grades with maximum toughness and ductility, the harder pearlitic grades for higher strength, the mixed ferritic-pearlitic grades for a multitude of intermediate applications, the molybdenum-containing grades for the best stress-rupture properties at elevated temperatures, the high-silicon grades for improved oxidation resistance, and other alloying combinations for low-temperature impact resistance. The automotive and agricultural implement industries are the major users of DI castings. The fact that DI castings are used for such critical automotive applications as crank shafts, front wheel spindle supports, and connecting rods is a testimonial to the high reliability and process economics associated with DI castings.

DI has graphite in the spheroidal form in the as-cast condition, a form which causes least interruption to the continuity of the metallic matrix and hence has the minimum detrimental effect on the matrix strength. In the as-cast condition, DI has strength much higher than gray cast iron. DI is a material with the product advantages of steel and the process advantages of cast iron. The striking growth and continued interest in the use of this material is due not only to its combination of a high tensile strength and measurable elongation in the as-cast condition but perhaps more due to the further improvement in the properties that can be brought about by heat treatment and also alloying. In recent years, there have been increasing attempts to replace steel forgings, steel castings, and gray iron castings by castings made of DI in applications involving aggressive environments. The selection of the material for any such application requires adequate data on the candidate materials under conditions of corrosion (Ref 1). Such data are not readily available for DIs, particularly for the low-alloyed ones especially under cold-worked conditions.

Repeated failures of a DI sewage rising main, after only three years' use, was investigated by Long (Ref 2). The combination of the high concentrations of inorganic sulfates, and the presence of sulfate-reducing bacteria normally found in domestic sewage, is believed to have resulted in the production of a large concentration of hydrogen sulfide which was then oxidized to sulfuric acid by air entrained at the pumping station. Fuji et al. (Ref 3) evaluated the extent of corrosion of DI pipe by using corrosion resistance based on A.C. impedance measurement method in solution containing many soluble components extracted from soil. Krawieca et al. (Ref 4) investigated the structure of the surface layer formed on austempered ductile iron (ADI) after exposure to hot concentrated sulfuric acid at the open-circuit potential value (OCP). The main elements of the surface layer are iron, silicon, oxygen, sulfur, and carbon. The erosion-corrosion wear characteristics and mechanism of martensitic ductile cast irons with different alloying compositions in quartz slurries with different pH values were determined and analyzed by Zhou et al. (Ref 5). The results indicated that the erosion-corrosion wear resistance of martensitic ductile cast iron would be increased not only with the pH values of the slurry and the erosion angle, but also with the addition of elements like copper, nickel, and chromium. Corrosion characteristics of vanadium-alloyed ductile cast iron in nitric acid at 30 °C was investigated by Aigbodion et al. (Ref 6). It was observed that addition of vanadium to ductile cast iron increased the corrosion resistance up to maximum of 0.25% V addition. This corrosion resistance is attributed to the formation of hard and passive phases which

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acted as strong protective barriers to corrosion. It was also observed that the rate of corrosion decreased with increase in the number of days of exposure, which was attributed to the deposition of corrosion products that tend to shield the corroding surface from further corrosion attack, thereby depressing the rate of corrosion. Corrosion studies involving austempered chilled ductile iron containing 0.1% Mo and Ni contents varying from 1.0 to 2.5% was carried out by Hemanth (Ref 7). The corrosion resistance was found to increase significantly with increase in Ni content and rate of chilling.

This article deals with the assessment of the corrosion behavior of unalloyed DI and alloyed DIs containing nickel, copper, and chromium. The corrosion data was generated by conducting electrochemical tests in natural sea water, 5 vol.% sulfuric acid, and 5 wt.% sodium hydroxide solutions.

2. Experimental

Castings (200 × 150 × 25 mm) of DI and DIs with 1 wt.% Ni, 1.0 wt.% Cu, 1 wt.% Cr were prepared by induction melting. The chemical analyses of these castings are given in Table 1. Strips of thickness 2 mm and width 20 mm were cut from these castings, and a sufficient number of them were annealed at 873 K for 2 h, and later acid pickled. These annealed strips were cold rolled to obtain 21% reduction in thickness. Circular coupons of 15 mm diameter were cut from (i) as-cast, (ii) annealed, and (iii) cold-rolled strips. All these coupons were metallographically polished. The polished coupons were used for polarization studies in natural seawater (pH = 8.1), 5 vol.% H_2SO_4 (pH = 0.2), and 5 wt.% NaOH (pH = 13.2) solutions. Open-circuit potentials (OCPs) during the first 90 min of exposure were recorded. Cathodic and anodic polarization of the samples were done using a scanning potentiostat (Versastat, EGandG, PARC). The effect of temperature on the corrosion rate was also studied by performing polarisation experiments at three different temperatures of 300, 325, and 340 K. The data analysis was carried out using 352 Softcorr^{TM} II software. The relative area percent of phases present was determined by point counting technique. A mean of the results of 10 trials performed on each of the samples was taken. The specimens were then subjected to corrosion studies.

A 3^3 factorial experiment (Ref 8) was carried out to study the effect of three factors, namely, specimen history (as-cast, annealed, 21% cold-worked), the medium and the temperature each at three levels, and their interaction on the corrosion behavior of DI. The main effects of these three factors on the corrosion rate are investigated. Factorial experiments were also conducted to study the effect of cold working (7, 14, 28%) and the composition of DI on corrosion rate. The corrosion rates of the unalloyed DI were compared with those of alloys 2 and 4. Alloys 2 and 4 contain Ni and Cr as alloying elements, respectively. The total sum of squares and the sum of squares due to each of the three factors were computed to assess the effect of various parameters on the corrosion rate.

3. Results and Discussion

The steady-state OCP data obtained for all the samples are summarized in Table 2. The corrosion rates measured at three different temperatures are given in Table 3. Table 4 shows the relative area percent of phases present in DIs. The typical results of the factorial experiments are given in Analysis of Variance (ANOVA) Table 5-9. The results of the analysis are summarized in Table 10 and 11.

It is known that DI generally has good corrosion resistance in many media. However, its corrosion resistance could be affected by alloying additions of elements like Cu, Ni, and Cr. On annealing, ferrite content increased (Table 4) by the decomposition of cementite into ferrite and free graphite. The alloying addition made is small, the changes in phase proportions are considerable, and hence alter the OCP values, and probably the primary passive potential (E_{pp}) and the critical current density ($i_{crit.}$) in a given medium. Alloying element Cu lowers the E_{pp} and decreases $i_{crit.}$ of DI (Ref 1), and makes the alloy undergo passivation rather easily. Table 2 shows that both Ni and Cu alloying additions shift the OCP under natural immersion to more positive values thus making the alloy more likely to enter into passive region. This was particularly observed in solutions with high pH (namely, sea water, and NaOH).

The alloying addition being small, the variation in the compositions of the film formed on DI, and alloyed DI may not be significant (Ref 9). However, the changes in the microstructure like the morphology and proportion of micro-constituents seem to have a significant effect on the inherent corrosion tendency of the material. Addition of copper increases the pearlite content of DI appreciably. This microstructural variation influences the corrosion resistance of the material. Cu is added to DI in special cases to increase the corrosion resistance to dilute acids, acid mine water, and atmospheric corrosion (Ref 10).

3.1 Corrosion in Sea Water

In sea water, the OCP values of unalloyed DI in the as-cast, stress relieved and cold-worked conditions were close to each other and shifted to more negative values with time. The increase in temperature resulted in the decrease of OCP. The cathodic reaction is hydrogen evolution reaction (HER) in acid

Table 1 Chemical composition of DI castings

	Composition, wt.%									
Alloy designation	**C**	**Si**	**S**	**P**	**Mn**	**Mg**	**Ni**	**Cu**	**Cr**	**Fe**
Alloy 1	3.12	2.21	0.02	0.11	0.44	0.02		…	…	Balance
Alloy 2	3.75	2.29	0.014	0.34	0.374	0.040	0.81	…	…	Balance
Alloy 3	3.12	2.21	0.02	0.11	0.44	0.02	…	0.70	…	Balance
Alloy 4	3.12	2.21	0.03	0.11	0.44	0.02	…	…	0.81	Balance

Table 2 Results of steady-state OCP measurements

Specimen history	Temperature of the medium, K	Steady-state OCP vs. SCE, mV											
		Alloy 1			Alloy 2			Alloy 3			Alloy 4		
		SW	SA	SH	SW	SA	SH	SW	SA	SH	SW	SA	SH
As-cast	300	−770	−585	−395	−740	−500	−505	−668	−500	−425	−755	−575	−455
	325	−785	−545	−385	−755	−460	−560	−675	−490	−435	−760	−570	−450
	340	−795	−510	−370	−765	−485	−360	−690	−495	−430	−770	−565	−425
Annealed	300	−760	−590	−360	−745	−500	−515	−670	−490	−387	−760	−545	−425
	325	−770	−560	−355	−770	−455	−415	−680	−413	−419	−760	−555	−421
	340	−780	−525	−345	−785	−475	−380	−695	−418	−406	−760	−540	−420
21% Cold worked	300	−760	−585	−420	−750	−530	−490	−675	−485	−380	−765	−560	−415
	325	−775	−545	−400	−760	−470	−440	−685	−475	−390	−775	−555	−410
	340	−790	−505	−385	−775	−480	−420	−700	−480	−385	−775	−550	−428

SW, sea water; SA, sulfuric acid; SH, sodium hydroxide

Table 3 Results of corrosion rate measurements

Specimen history	Temperature of the medium, K	Corrosion Rates, mm/year											
		Alloy 1			Alloy 2			Alloy 3			Alloy 4		
		SW	SA	SH	SW	SA	SH	SW	SA	SH	SW	SA	SH
As-cast	300	0.6096	22.200	0.1219	0.4826	5.1310	0.0356	0.4826	11.180	0.0838	0.5588	5.3590	0.1067
	325	1.4224	54.585	0.1651	1.0668	6.6290	0.0838	1.3208	46.960	0.1549	0.8890	7.1120	0.1626
	340	2.0066	79.959	0.1878	1.7780	7.6200	0.1600	1.8796	74.625	0.1829	1.3208	13.055	0.1829
Annealed	300	0.5842	22.072	0.1168	0.5080	5.4356	0.0508	0.4572	10.973	0.0813	0.4572	2.1082	0.0381
	325	1.3970	51.257	0.1626	1.1176	7.4422	0.0864	1.2446	43.612	0.1448	0.8636	6.9342	0.1168
	340	1.9812	76.632	0.1854	1.8034	10.465	0.1626	1.8013	71.272	0.1803	1.2954	12.751	0.1803
21% Cold worked	300	0.7620	24.994	0.0940	0.5080	4.8260	0.0813	0.6604	1.3716	0.0864	0.6604	2.1590	0.0457
	325	1.3970	28.016	0.1422	1.2700	6.9596	0.1270	1.4220	27.026	0.1270	0.9144	7.4168	0.1067
	340	2.1590	33.757	0.1600	1.9050	12.014	0.1499	1.9812	27.762	0.1499	1.3462	14.249	0.1372

SW, sea water; SA, sulfuric acid; SH, sodium hydroxide

Table 4 Microstructural analysis of the DIs

Alloy No.	History	Relative area percent of phases		
		Pearlite	Ferrite	Graphite (Balance)
Alloy 1	As cast	60	28	12
	Annealed	49	38	13
	21% C.W.	46	41	13
Alloy 2	As cast	56	31	13
	Annealed	55	32	13
	21% C.W.	50	37	13
Alloy 3	As cast	86	03	11
	Annealed	76	12	12
	21% C.W.	74	14	12
Alloy 4	As cast	70	18	12
	Annealed	60	27	13
	21% C.W.	58	29	13

Table 5 Typical ANOVA table for corrosion potential—Alloy 1

Source	Sum of squares (S.S.)	Degrees of freedom (D.F.)	Mean square (M.S.)	Test statistic (F_0)
History (A)	890.7	2	445.4	24.4
Medium (B)	712679.6	2	356339.8	19485.9
Temp. (C)	2690.7	2	1345.4	73.6
AB	3270.4	4	817.6	44.7
AC	59.3	4	14.8	0.8
BC	7253.7	4	1813.4	99.2
Error	146.3	8	18.3	
Total	726990.7	26		

medium whereas in the other two media it is oxygen reduction, and the corrosion reaction is under cathodic control. In the as-cast condition, the relative area percent of pearlite is more as compared with annealed or cold-worked conditions. Further, the corrosion resistance of phases is in the order graphite > ferrite > pearlito-ferrite > pearlite (Ref 11, 12). Therefore, DI in the as-cast condition shows a higher corrosion rate than that in annealed condition, since pearlite is the least corrosion resistant. Porosity present in the as-cast DI also can degrade its corrosion resistance (Ref 10). Annealing of DI reduces its pearlite content. Cold working generally increases the corrosion rate because of increased stored energy and dislocation density (Ref 13), and variation in crystallographic orientation, and morphology of phases. It is also reported (Ref 14) that in steels,

Table 6 Typical ANOVA table for corrosion rate—Alloy 2

Source	Sum of squares (S.S.)	Degrees of freedom (D.F.)	Mean square (M.S.)	Test statistic (F_0)
History (A)	2344.2	2	1172.1	1.4
Medium (B)	432683.5	2	216341.8	255.1
Temp. (C)	31445.5	2	15722.7	18.5
AB	3796.2	4	949.0	1.1
AC	3332.6	4	833.1	1.0
BC	29573.4	4	7393.3	8.7
Error	6784.0	8	848.0	
Total	509959.3	26		

Table 7 ANOVA table for Alloy 3—cold-working effect

Source	S.S.	D.F.	M.S.	F_0
A (Cold working)	697099.6	2	348549.8	6.615091
B (Medium)	7837303	2	3918651	74.37169
C (temp.)	586042.2	2	293021.1	5.561218
AB	1337170	4	334292.4	6.344502
AC	212785	4	53196.35	1.0009608
BC	1001420	4	250355	4.751462
Error	421520.8	8	52690.1	
Total	12093341	26		

Table 8 Typical ANOVA table for Alloys 1, 2, and 4 (as-cast) samples

Source	S.S.	D.F.	M.S.	F_0
A (Composition)	2107458	2	1053729	8.71
B (Medium)	4416701	2	2208350	18.25
C (temp.)	442593	2	221296	1.83
AB	4114371	4	1028593	8.50
AC	492339	4	123084	1.02
BC	754065	4	188516	1.56
Error	967850	8	120981	
Total	13295377	26		

Table 9 Typical ANOVA table for Alloys 2, 3, and 4 (annealed) samples

Source	S.S.	D.F.	M.S.	F_0
A (Composition)	1237162	2	618581	5.17
B (Medium)	3160097	2	1580048	13.20
C (temp.)	547661	2	273830	2.29
AB	2438470	4	609617	5.09
AC	483015	4	120753	1.01
BC	947262	4	2368156	1.98
Error	957597	8	119699	
Total	9771264	26		

Table 10 Results of the analysis for Alloys 1, 2, and 4

	Annealed	As cast	Cold worked
Composition (A)	S	S	S
Medium (B)	S	S	S
Temperature (C)	N	N	S
AB	S	S	S
AC	N	N	N
BC	N	N	N

S, significant; N, not significant

Table 11 Results of the analysis for Alloys 2, 3, and 4

	Annealed	As cast	Cold worked
Composition (A)	S*	S*	S
Medium (B)	S	S	S
Temperature (C)	N	N	S
AB	S	S	S
AC	N	N	N
BC	N	N	S

S, significant; N, not significant; *, not significant at 1% level

the increase in corrosion rate on cold working is by precipitation of carbides, or nitrides, or both at imperfection sites, which establishes local corrosion cells. This may be true in the case of DI also, as its matrix microstructure is similar to that of steels. Cold working alters the morphology of nodular graphite, the spherical shape changing over to elongated and irregular shape. Although, the graphite shape is critical for mechanical properties, it does not have a strong effect on corrosion resistance. The proportion of the phases in the matrix on the other hand has a slight influence on the corrosion resistance.

The effects of both the potential and pH on the corrosion tendency of DI can be seen qualitatively from potential-pH (Pourbaix) diagram (Ref 1) for Fe-H_2O system. The OCP and pH values indicate unalloyed DI to corrode in sea water in the as-cast, annealed, and cold-worked conditions. Increase in the temperature increased the corrosion rate of DI in all the three conditions in sea water because of the increased kinetics of metal dissolution, and higher diffusion rates of oxygen. The corrosion resistance of unalloyed DI is in the order: annealed > as-cast > cold worked.

The corrosion rates for Alloy 2 are less than those for Alloy 1 for all the experiments (Table 3). The higher corrosion resistance observed in the case of Alloy 2 is obviously due to the protective film-forming tendency developed on alloying with Ni (Ref 10). The stability, adherence, strength, and repassivation characteristics of the nickel oxide film are dependent on the substrate surface and alloy composition, and this can account for slight variations in the corrosion rate under different conditions of the alloys, viz., as-cast, annealed, and cold worked. Since the variation of OCP with time was similar to that observed for Alloy 1, and the effect of temperature on the corrosion rate of Alloy 2 also being similar to Alloy 1 in sea water, it is concluded that the cathodic reaction is oxygen reduction, and the corrosion reaction is under cathodic control.

In iron and steel, carbon, whether it exists as graphite or as carbide, is more noble than iron matrix (Ref 15); the e.m.f. of graphite-to-ferrite cell being as high as 2 volts (Ref 16).

The shape, size, and distribution of graphite are important since corrosion tends to penetrate along the boundary of the graphite particles (Ref 17). The rate and extent of such penetration is less when graphite occurs as discrete spheroids with random distribution (Ref 11). Graphite is insoluble in most of the environments and, as corrosion proceeds, it will be left as a residue adhering more or less firmly to the as-yet unattacked iron beneath. The firmness of attachment and compactness or permeability of the nodule in DI is influenced by strengthening effects of other insoluble constituents or corrosion products such as oxycompounds that may be present in the immediate vicinity. The intermixing of these can become so impermeable to further penetration, and the corrosion rate can be considerably low (Ref 11, 18). The visual examination of the corroded surface showed uniformly distributed rust. Since oxygen reduction could be the major cathodic reaction in sea-water corrosion of these irons, it is likely that a surface film of oxycompounds of Cu (Alloy 3) could be formed on alloyed DI on the surface, which is also corrosion resistant and hence cause the decrease in the corrosion rate of Alloy 3 as compared to Alloy 1 (Table 3).

Chromium is carbide former and pearlite stabilizer. Chromium addition refines graphite and matrix microstructure. These refinements enhance the corrosion resistance of DI in sea water by the formation of protective oxide film on the surface.

Alloy 4 showed steady-state OCP to be more or less the same as compared with unalloyed DI. The potential shifts in the negative (active) direction in sea water with time and increase in temperature made the OCP values more negative under all conditions of the material (Table 2). The cathodic reaction is mainly oxygen reduction.

The corrosion rates of Alloy 4 were marginally less than those of unalloyed DI under all conditions of the material. However, at higher temperatures, Alloy 4 had better resistance than Alloy 1. The corrosion rates were comparatively lower because of the strong tendency of the metal chromium to form protective oxide film on the surface of the alloy, under oxidation conditions. The cold working of the materials increased the corrosion susceptibility. The increase in stored energy and dislocation density on cold working helps in initiating corrosion process and delaying the formation of a stable compact surface film. Increase in the temperature increased the corrosion rate (Table 3) as in the case of Alloy 1.

3.2 Corrosion in Sulfuric Acid

The OCP for as-cast, annealed, and cold-worked DI at all the temperatures increased with time. The cathodic reaction is primarily hydrogen evolution reaction. The values of corrosion rates are higher. The higher rate of corrosion in acid medium is due to several contributing factors such as dissolution of corrosion product at the interface, non-formation of a surface film at low pH, high exchange current density for hydrogen evolution, low hydrogen overvoltage, and also the availability of dissolved oxygen for reduction. As the temperature can affect the above factors, increase in temperature will markedly increase the corrosion rates (Table 3).

Corroded samples showed a localized attack around the nodules resulting in the loosening and falling off of graphite nodules. The corrosion tendency near the nodule can be explained on the basis of the fact that spheroidal graphite (more noble) surrounded by ferrite (more active) forms a galvanic couple.

The sequence of observed corrosion resistance of DI in sulfuric acid medium is: annealed > as-cast > cold-worked conditions. This can be explained on the basis of microstructure. It is reported (Ref 11) that DI is generally considered superior to gray iron, and ferritic matrix irons are superior to pearlitic matrix irons in acid medium. This explains the difference in the corrosion behavior in the as-cast and annealed conditions. In the case of alloyed DI, the OCP increased with time, and the steady-state potentials were nobler than that of the unalloyed DI (Alloy 1). Increase in temperature increased the steady-state OCP to more noble values.

In the case of Alloy 2, the OCP shifts in the noble direction with time. The effect of temperature on the OCP is to shift the potential to more positive values. This may be due to the increased polarization of the anode or the depolarization of the cathode. Compared to unalloyed DI, this alloy has more noble OCP values in H_2SO_4 medium because of alloying with nobler Ni (Table 2). The corrosion behavior of this alloy in this medium is very similar to that in sea water except that the corrosion rates are very much higher because of instability of surface oxide film under acidic condition. As described earlier, the corrosion rates in the as-cast, annealed and cold-worked conditions of Ni-alloyed DI are different because of the changes in the relative area percent of constituents. As the surface film is unstable, both the metal dissolution rate as well as the rate of the primary cathodic reaction (the hydrogen evolution reaction) can be high.

The corrosion rates of Alloy 3 were less than those of Alloy 1. It is reported that Cu-bearing steels also were found to corrode in non-oxidizing acids at lower rates than Cu-free steels. Cu counteracts the accelerating effects of P and S (Ref 14). The beneficial effect of Cu in low alloy steels is also because of its positive electrochemical potential. It can plate out on the surface of iron as elementary Cu (cathodic inclusions) in accordance with cathodic depolarization reaction (Ref 13),

$$Cu^{2+} + 2e^- = Cu.$$

In addition, the layer of corrosion products becomes more compact and denser. It is less hydrophilic in nature and has better protective properties than that of Cu-free DIs in acid medium. Also, Cu dissolved in DI decreases the exchange current of the cathodic reaction in sulfuric acid, thereby decreasing the corrosion rate (Ref 19).

As in the case of Alloy 1, the sequence with respect to the corrosion resistance of Alloy 3 is in the order: annealed > as-cast > cold worked. Increase in temperature increased the corrosion rate under all conditions.

For alloy 4, the OCP values stabilized quickly. With increase in temperature, the potential shifted to more noble side with time thereby showing enhancement of anodic control with rise in temperature. The steady-state OCP values were almost the same as those for Alloy 1 for all the conditions of the alloy and at all the temperatures of the medium (Table 2). Chromium, being a metal of lower thermodynamic stability, does not make the matrix nobler. With rise in temperature the steady-state OCP values became more positive under all the conditions of the material similar to Alloy 1.

There was considerable improvement in the corrosion resistance of DI by the addition of Cr. In most cases of acid corrosion, graphite has a negative influence on corrosion resistance especially in non-oxidizing acids. In a Cr-alloyed DI, the reduction in the quantity of graphite in the structure is accompanied by increased cementite content which is desirable from the corrosion point of view. Further, Cr increases the tendency of metals and alloys to passivate easily in aqueous acid media (Ref 20). On annealing, the corrosion rate was found to decrease. This is because some cementite in pearlite in the as-cast structure had broken down into ferrite and graphite (Table 4). In such pearlito-ferritic iron, the combined carbon (cementite) has little influence on corrosion. As ferrite structure is more resistant in acid media, increasing of ferrite content by annealing will lower the corrosion rate justifying the observed phenomenon.

The effects of temperature and cold work were the same as those observed in sea water for this alloy. The corrosion rate decreased as compared with Alloy 1, but the rate was still high and the sequence with respect to corrosion resistance is the same as that for Alloy 1 in sulfuric acid.

3.3 Corrosion in Sodium Hydroxide

The OCP became nobler with time for as-cast, annealed, and cold-worked DI at all the temperatures studied. At higher temperatures, the potential values were nobler. The principal cathodic reaction is oxygen reduction.

DIs, like steels, generally exhibit good corrosion resistance to alkalis. Dilute alkalis do not attack DI at low temperatures. Increase in temperature by 40 K will not appreciably increase the corrosion rate. The material shows passivity as pH is also high. This can be seen from the Pourbaix diagram. The surface film is strong and adherent. The repassivation kinetics are better as the oxide phase is stable (Ref 1).

Alloy 1 shows a tendency to passivate, irrespective of its condition, in NaOH. It thus shows low and similar corrosion rates in the as-cast, annealed and cold-worked conditions. The variation of OCP with time is similar to that in H_2SO_4. Increase in temperature initially shifted the potential in noble direction. However, at higher temperatures, OCP shifted to the active direction. The corrosion rates (Table 3) in NaOH medium were the least under all the conditions of the material and temperatures of the medium because of strong passive film on the surface. The sequence of corrosion resistance is in the order: annealed > as-cast > cold worked.

In the case of alloyed DIs, the OCP values were shifted toward noble side with time indicating the tendency toward anodic control. With respect to temperature, no specific comment can be made on the variation of steady-state potential (Table 2). The steady-state OCP values in alkaline medium were almost similar for both unalloyed DI, and alloyed DI. The variation of corrosion resistance, though almost insignificant with the condition of the alloy, the order of corrosion resistance for various alloys obtained in sulfuric acid medium holds good in this case also. The temperature rise increased the corrosion rate marginally. The high corrosion resistance observed in alkaline medium is due to the microstructure which forms a protective stable oxide surface film. The addition of alloying elements alters the phase proportions, and helps in the formation of a denser, more adherent, and stronger oxide film on the surface.

3.4 Factorial Experiments

From F-tables for potentials (Table 5), it is seen that $F_{0.05,\ 2,\ 8} = 4.46$, and $F_{0.05,\ 4,\ 8} = 3.84$. The analysis indicates that the medium is the significant factor influencing the corrosion potential for all alloys. History also had a significant effect on the corrosion potential, except in DI alloyed with Ni. This could be attributed to the formation of a passive film on DI alloyed with Ni. Table 2 shows that Ni shifts the OCP under natural immersion to more positive values, thus making the alloy more likely to enter into passive region, more so in solutions with high pH (namely, sea water and NaOH).

Temperature has a significant effect only in Alloy 1. The interaction effect AB (History + Medium) had a significant effect on corrosion potential except in Alloy 4. The interaction effect AC (History + Temp.) was not significant for all the alloys. The effect BC (Medium + Temp.) had significant effect on all DIs except in Alloy 1 and Alloy 4.

The ANOVA tables constructed using the linear polarization data for corrosion rates (Table 6) indicated that the effect of specimen history on corrosion rate was not significant whereas both the medium and temperature had a significant effect. The interaction effect BC (Medium + Temp) was significant. The effects of other interactions are not significant. The main effects of specimen history, medium, and temperature on the corrosion rate indicated that the effect of specimen history on corrosion rate is not significant as compared to the medium and temperature.

ANOVA table (Table 7) constructed using the corrosion data on specimens subjected to different degrees of cold working indicated that the specimen history and the medium had a significant effect on the corrosion rate. The effect of temperature on the corrosion rate was also significant except in Alloy 1. Alloy 1 has a higher corrosion rate. Hence, the effect of temperature was insignificant. The interaction effect AB (history + medium) was significant except in Alloy 4 (alloyed with Cr). The effect AC (history + temp) was not significant. BC (medium + temp) was a significant interaction effect except in the case of Alloy 1. Factorial experiments also suggested that the effects of temperature and composition on corrosion rates of cold worked samples were more significant as compared to the effect on annealed and as-cast samples.

4. Conclusions

1. Both unalloyed and alloyed DIs possess the highest corrosion resistance in sodium hydroxide solution, the lowest in sulfuric acid, and intermediate in sea water.
2. Alloyed DIs, whether as-cast, annealed or cold worked, have better corrosion resistance than the unalloyed ones in all the three media, and the temperatures studied.
3. The microstructure of the alloy is found to have an effect on the corrosion properties. The shape, size, and distribution of carbon also affect the corrosion rate though not significantly.
4. Annealing improves the corrosion resistance of DIs (both alloyed, and unalloyed). The corrosion resistance in most of the cases is in the order: slightly cold worked > annealed > as-cast > severely cold worked.
5. Corrosion potential is influenced by the medium. Specimen history had a significant effect on the corrosion potential except in DI alloyed with Ni. The temperature influences the corrosion potential only in unalloyed DI.
6. When the specimens were subjected to different levels of cold working, the corrosion rate was influenced by both the history and the medium. Temperature also had a

significant effect on the corrosion rate except in the case of unalloyed DI. Alloying DI with Ni and Cr significantly influences corrosion rate for all the histories. Temperature is found to have a significant effect on the corrosion rate in the case of cold-worked samples.

7. Factorial experiments carried out for various DI subjected to treatments indicated that the cold-worked samples were more sensitive to the effect of temperature and composition on the corrosion rate as compared to the annealed and as-cast samples. The medium had a significant effect on the corrosion rate in all the cases.

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