CORROSION RESISTANCE OF WHITE CAST IRONS IN CAUSTIC SOLUTIONS

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Abstract

High chromium white cast irons have proven to be a useful family of materials for wear resistant applications in high temperature Bayer liquor, as they combine high abrasion resistance with reasonable corrosion resistance. Plant experience has shown that certain alloy grades exhibit poor performance in high temperature applications at the end of the digestion circuit and it has been suggested that this is related to the corrosion resistance of these materials. In this paper, the corrosion behaviour of three grades of high chromium white cast iron was studied in pure caustic solutions at temperatures from 170°C to 280°C, with exposure times of up to 57 days. It was found that at lower temperature, the corrosion proceeded by a mechanism of degradation of the carbide-matrix interface with significant corrosion of the carbide component of the alloy. At higher temperatures, preferential corrosion of the matrix occurred in lower alloy grades, leaving carbide particles exposed to mechanical damage whilst in higher alloy grades, corrosion occurred by corrosion penetration along the carbide-matrix boundary. Corrosion resistance also correlated with the microstructure of the alloys and a number of the alloy constituents, including chromium content. This work will assist in our understanding of the mechanism of degradation of white irons in Bayer liquor and in the selection of white cast iron grades for application in high temperature digestion circuits.

1. Introduction

White cast irons are a valuable material for combating wear in the minerals industries and have been used extensively in applications where abrasion resistance is important [1,2]. High chromium white irons have been developed over a number years for these types of applications, as the discontinuous carbide morphologies provide the iron with relatively high fracture toughnesses [3-5]. In addition, the high chromium contents have also meant that the white irons are corrosion resistant and this combination of corrosion resistance and wear resistance has made high chromium white irons a material of choice for a number of industries [6-10].

In alumina refining, bauxite is processed in process fluids that contain high levels of caustic soda and at elevated temperatures. Under these conditions, materials will often see slurry wear occurring under highly corrosive situations. The maximum digestion temperature for bauxite processing depends on the quality of the bauxite, but as bauxite grades become richer in silicates and monohydrates, higher digestion temperatures are required and some modern refineries operate with digestion temperatures up to 280°C.

This series of studies was initiated in response to the rapid degradation of some white iron types used as part of isolation valves at the high temperature section of the digestion circuit of a refinery. The maximum operating temperature of the refinery was 280°C. A metallurgical failure analysis of the white irons suggested that although the failure mechanism appeared to be wear related, the failure was significantly influenced by corrosion of the alloys [11]. Deep corrosion of the matrix of the alloys was observed, leaving carbide particle loosely supported in oxide material. It was postulated that the mechanism of degradation was primarily corrosion related, with the wearing particles in the slurry eroding away loose oxide and fracturing the exposed carbide particles. As a result, a series of studies was initiated to investigate the corrosion behaviour of some white irons in high temperature caustic solutions.
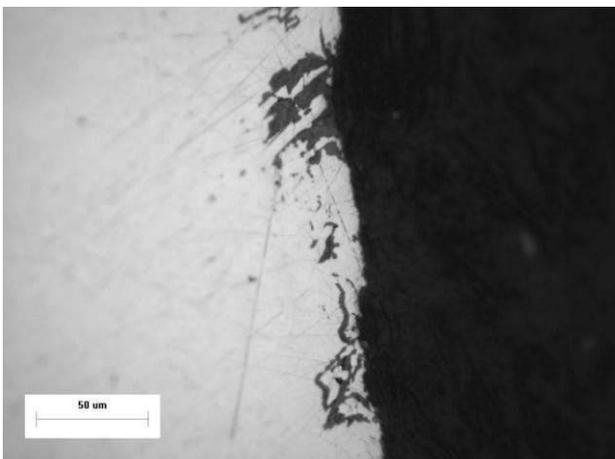

Figure 1 Failure of the white iron components in service was in part the result of corrosion, particularly of the matrix of the alloy (from).

2. Materials and Methods

Three alloy types were used in this study. All alloys were high chromium white cast irons, but had different compositions, particularly with regards to Cr and Mo contents. A summary of the alloy compositions are as shown in Table 1. Each of the alloys consisted of M_7C_3 type carbide particles in a steel-type matrix (see Figure 2). The matrix of the Type 1 alloys consisted of pearlite and martensite whilst the matrix for the Type 2 and Type 3 alloys consisted of martensite alone. Both types of matrix showed evidence of precipitation of secondary carbide particles. The compositions of the microconstituents were analysed using energy dispersive spectroscopy (EDS) in a JEOL JSM 6360 LA scanning electron microscope (SEM) and the results of the analyses are as shown in Table 2.
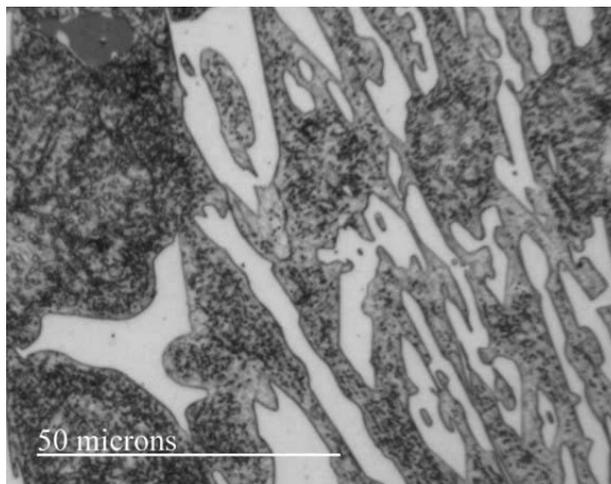

Figure 2 Typical microstructure of the Type 3 alloy.

Table 1   Compositions of the three types of white iron used in the testing (Weight %).

Sample No	Fe%	C%	Mn%	Si%	S%	P%	Ni%	Cr%	Mo%	Cu%
Type 1	Bal	3.22	1.55	0.47	0.02	0.02	0.12	16.0	0.02	1.02
Type 2	Bal	2.97	1.33	0.47	0.02	0.02	0.14	20.3	0.46	1.02
Type 3	Bal	2.78	1.29	0.47	0.02	0.02	0.15	23.2	1.10	0.90

Table 2   Approximate composition of the matrix and carbide particles, as determined by EDS (Atom %) (major elements only).

Sample No	Matrix Composition (at%)					Carbide composition (at%)				
	Fe%	Si%	Cr%	Mo%	Cu%	C%	Fe%	Mn%	Cr%	Mo%
Type 1	Bal	1.3	7.7	0.04	1.1	23.7	34.6	1.6	37.1	0.1
Type 2	Bal	1.1	8.0	0.2	1.1	25.6	27.4	1.7	43.1	0.2
Type 3	Bal	1.1	14.0	1.1	1.1	23.4	27.5	1.2	46.7	1.0

Corrosion testing was carried out under free potential conditions in a stainless steel PARR autoclave. The samples were approximately 5 g in weight and one surface of each sample was polished to a metallographic finish prior to testing. The samples were placed into the autoclave on a Teflon base to insulate them from the container such that the polished side was uppermost. All tests were carried out using a solution of 110 g NaOH per litre.

Three samples of each of the three alloy types were placed in the autoclave for each test, along with approximately 300 ml of caustic solution. New solution was used for each test. The samples were then heated in the autoclave for 10 days at the exposure temperature. Five test runs were carried out in this series of tests and the test temperatures were: 170°C, 200°C, 220°C, 250°C and 280°C. Once the solution was cooled, the samples were removed and washed in distilled water prior to examination.

Samples were first examined on the corroded surfaces in order to study the oxide morphologies and compositions. This was done using the SEM and the compositions of the oxides were measured using EDS. Samples were then cut through the oxide to study the cross-sectional behaviour of the corrosion. These samples were mounted in Bakelite and prepared to ASTM E3 prior to examination. The crossections were examined in the unetched state using SEM and further measurements of the oxide composition were made using EDS. Cross-sectional samples were also etched after polishing using Vilella's reagent to determine the microstructural features of the corrosion.
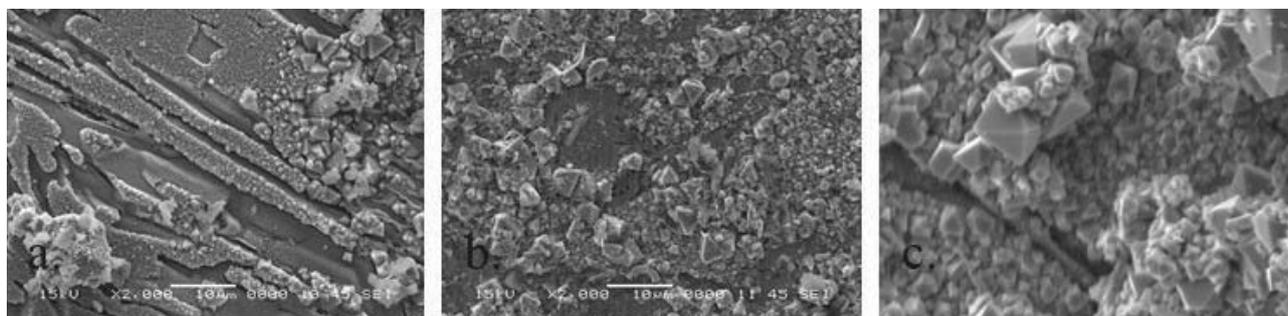

Figure 3 a, b and c. Effect of exposure temperature on the morphology of surface oxides for Type 2 alloy. a. 170°C, b. 220°C and c. 280°C.

3. Experimental Results

All samples examined showed some evidence of corrosion, although the corrosion on the sample exposed at 170°C was relatively slight when compared with samples tested at higher temperatures. Weight loss measurements were not able to provide useful data on the relative corrosion behaviour of the alloys. Therefore, characterisation of the corrosion behaviour relied on the morphological characterisation and characterisation of the metallographic sections.

Examination of the corroded surfaces of the samples, particularly at the lower temperatures, indicated that the oxide type that formed on areas of carbide was morphologically different to that formed on the matrix material. Oxide particles over the matrix material showed a strong octahedral habit, typical of (FeCr) spinel crystals. These can be seen in Figure 3a-c. Also in Figure 3a-c, it can be seen that the oxide associated with the carbide particles was less faceted. At higher temperatures there was less distinction between the different types of oxide, possibly as the oxide tended to grow more rapidly at higher temperatures. Also, in general, the spinel crystals tended to be larger.
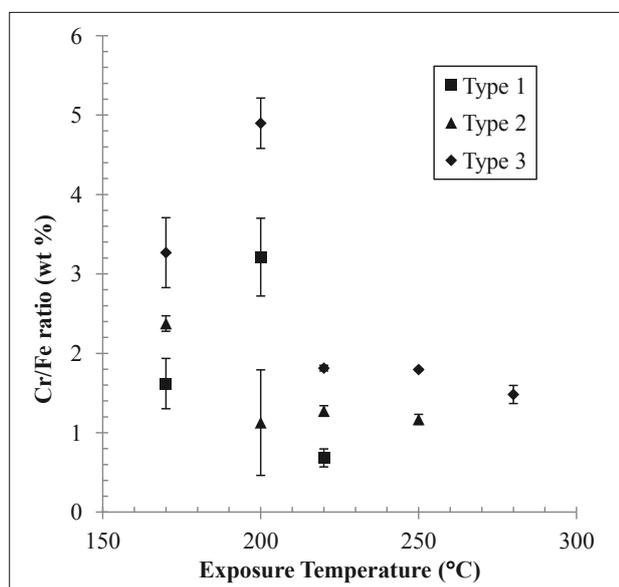

Figure 4 Effect of exposure temperature on the Cr/Fe ratio in the oxide above the carbide particles. Error bars represent standard error of the measurements.

The chromium to iron ratios of the surface oxide was measured using the EDS data for oxide formed on matrix material and carbide material. The results for the carbide particles are as shown in Figure 4, the oxide that formed at lower temperatures appeared to be enriched in Cr when compared with the Cr/Fe ratio in the carbides in the matrix. For the Type 1 alloy, the Cr/Fe ratio was approximately 1, and for the Type 2 and 3 alloys, the Cr/Fe ratio was 1.5 to 2. At higher temperatures, the Cr content of the oxide appeared to decrease.

Similar trends were observed for the matrix material. The highest Cr/Fe ratios were observed at the lower exposure temperatures and this appeared to stabilize around 0.3 at higher temperatures. Again, this is significantly higher than the Cr/Fe ratio in the uncorroded alloy matrix, suggesting that the corrosion process enriches the oxide in Cr. The results of this testing can be seen in Figure 5.
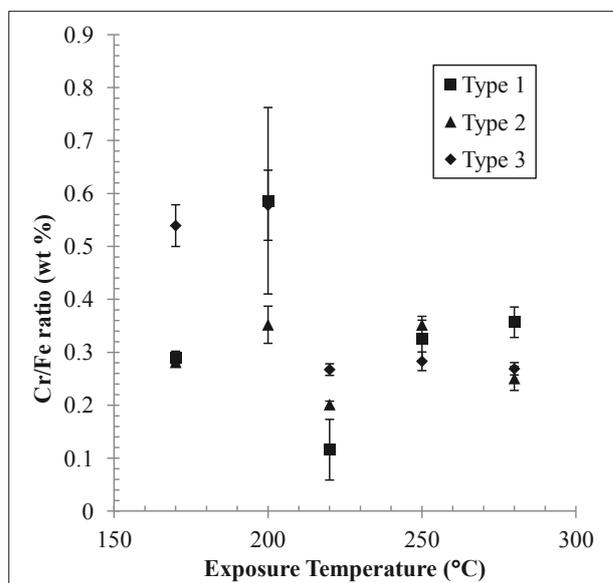

Figure 5 Effect of exposure temperature on the Cr/Fe ratio in the oxide above the matrix material. Error bars represent standard error of the measurements.

Examination of the metallographic cross-sections of the corroded samples showed several interesting trends regarding the progress of the corrosion. At lower temperatures, the corrosion tended to follow the carbide-matrix interphase boundary. This also led to some preferential corrosion of the carbide particles. This is in line with previous experience in the corrosion of steels and white irons, where the preferential corrosion of carbide particles was reported [12, 13]. However, at elevated temperature, the situation was reversed and the carbide particles appeared to corrode more slowly than the matrix, leaving the carbides poorly supported in the matrix and vulnerable to fracture. This was particularly noticeable in the field failures examined, but could also be seen in the laboratory samples. These trends can be seen in Figure 6. A comparison of the three different alloys, however, did not reveal significant differences in behaviour in the laboratory studies, despite some anecdotal differences in field performance. The temperature at which the change from carbide corrosion to matrix corrosion occurred was approximately 250°C.

4. Discussion

This study has shown a number of interesting outcomes regarding the corrosion of white irons in caustic solutions. Although testing was not carried out in Bayer liquor, the results have demonstrated the effects of concentrated caustic on the corrosion behaviour of white cast irons and the damage observed in this work has mirrored that observed in field samples.

The results indicate the importance of exposure temperature on the mechanisms of corrosion damage in the white irons. At low temperature degradation proceeded predominately by corrosion of the carbide particles and the interphase boundaries. However, at temperatures above 250°C, the corrosion occurred predominantly in the matrix material, with little interphase boundary penetration.
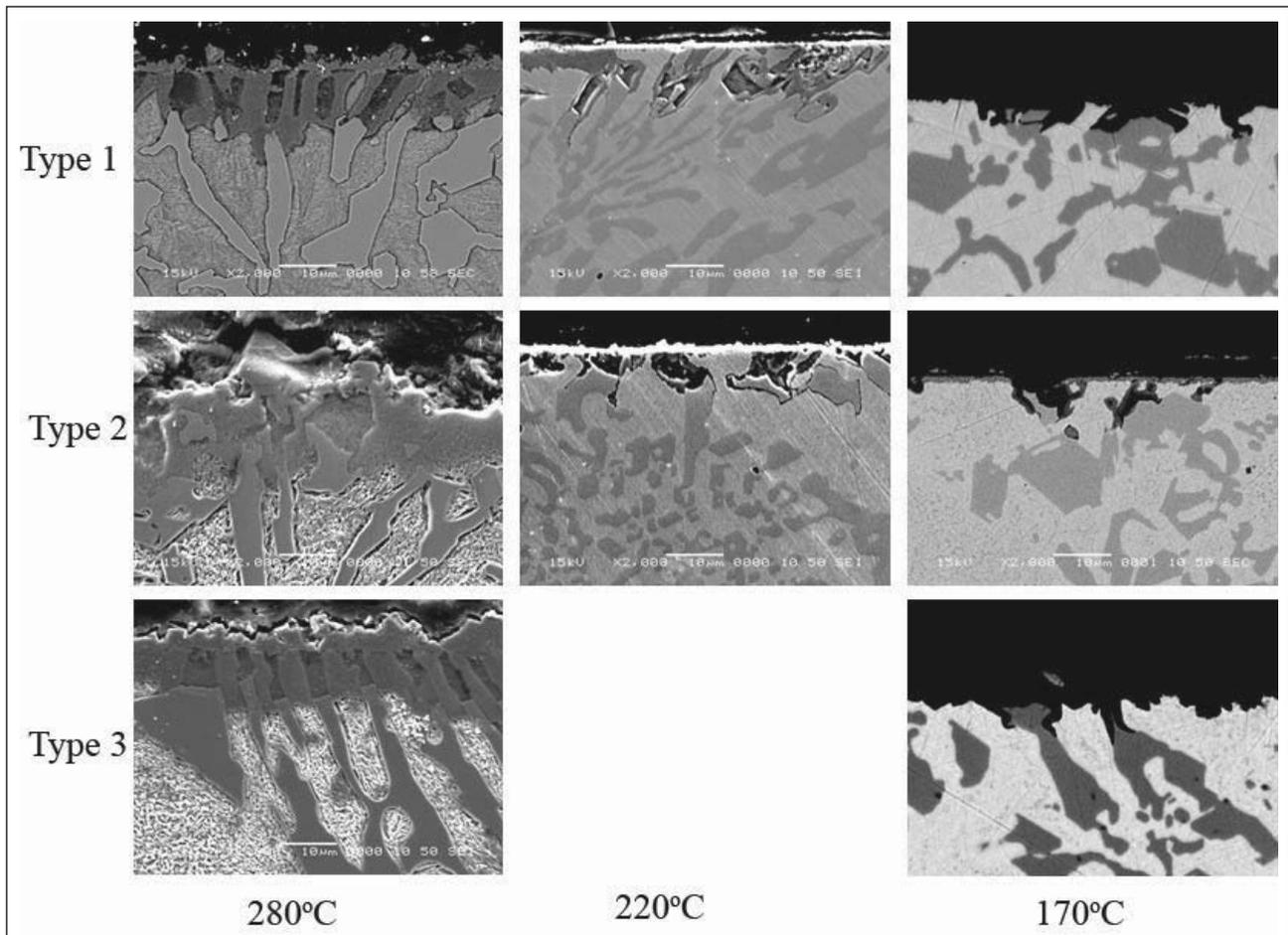
Figure 6 Effect of exposure temperature and alloy type on the corrosion behaviour of the alloys.

Both cases have implications for the resistance of the alloy to wear. In the case where corrosion is occurring predominantly in the carbide (i.e. low temperatures), the wear resistance of the alloy is likely to be determined by a combination of the corrosion rate of the carbide particles and the wear rate of the matrix. In this case, improvements in matrix hardness may have a significant effect on the wear rate. At elevated temperatures, however, it is likely that matrix corrosion rate may be a greater influence on wear resistance. Once the carbide particles are exposed and unsupported, it is likely that they will break off and play no further part in the resistance of the alloy to wear. These results have implications for alloy design for white irons in particular conditions in the refinery.

The reason for this change in corrosion behaviour has not been established. Corrosion of multiphase alloys often proceed as a result of differences in electrochemical potential between the phases and this can lead to micro-galvanic corrosion cells being established. One possible reason for the change in behaviour may be that the relative electrochemical potentials of the carbides and matrix components of the alloys changed with test temperature. This has yet to be fully investigated.

At lower temperatures, it appeared that the oxides associated with carbide particles had quite high Cr/Fe ratios and that the Cr content of the oxide had been enriched when compared with that of the uncorroded carbide. At higher temperatures, it was more difficult to distinguish between the oxide on carbide and the oxide on matrix, but the oxides were characterized by lower Cr/Fe ratios that those observed at higher temperatures. However,

this may be because the oxide films of samples exposed at 170°C were less mature than those produced at 280°C. All samples were produced at 10 days. However, earlier work at 250°C had been carried out in order to study the effects of exposure time on corrosion behaviour [14].

This work [14] showed that the octahedral crystals formed rapidly on the surface of the alloy but over time changed morphology. Although well-defined initially, the octahedral spinel crystals gradually became more highly twinned and the oxide converted from a relatively low Cr content, predominantly octahedral form to a higher chromium content background matrix. Significant morphological and compositional changes were observed in the oxide films over exposure time periods from 1 to 57 days. Work is continuing to investigate the effects of exposure time on the corrosion behaviour.

5. Conclusions

Corrosion of three types of high chromium white cast iron was studied at temperatures from 170°C to 280°C. It was found that the mechanism of corrosion changed from corrosion predominantly of the carbide particles at lower temperatures to corrosion predominantly of matrix material at higher temperatures, with a change over temperature of approximately 250°C. Furthermore, it was demonstrated that enrichment of the oxide film with chromium occurred when compared with alloy compositions, and that this enrichment was strongest at lower exposure temperatures. These results have implications for the design of white iron alloys for resistance in concentrated caustic solutions.

6. Acknowledgements

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