



The Influence Of Microstructure On The Corrosion And Wear Mechanisms Of High Chromium White Irons In Highly Caustic Solutions

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Abstract

High chromium white irons are used extensively for wear resistance applications and owing to their high chromium content are often used in erosive-corrosive environments such as alumina processing plants using the Bayer refining process. The first stages of the Bayer refining processes (the red side) involve the transfer of hot slurries containing a high proportion of erosive quartz particles suspended in a pH 14 caustic solution. The solution contains varying amounts of dissolved alumina making the environment erosive and corrosive. High chromium white irons are often used to prolong service life and reduce operating costs. Pump components are often cast high chromium white irons and piping is often weld overlaid with high chromium white iron. To date there has been very little information reported in the literature on the wear of high chromium white irons in alumina processing environments. Furthermore, very limited work has been reported on the corrosion behaviour of high chromium white irons in caustic environments.

This thesis investigates the development of microstructure in high chromium white irons typically used in the Australian Alumina Industry and how variables such as the bulk chemical composition, cooling rate and heat treatment can be used to vary the microstructure. Microstructural characteristics that influence wear and corrosion were investigated by undertaking corrosion and erosion-corrosion wear tests in a sodium aluminate solution representative of what is found in the alumina processing industry. The corrosion of high chromium white irons in sodium hydroxide solution was compared with their corrosion in sodium aluminate solution to investigate the influence aluminate ions have on corrosion.

A range of ex-service alumina processing plant high chromium white irons castings and weld overlays were investigated. This not only provided materials for further testing but from the examination of the wear surface allowed the results of laboratory wear tests to be compared with those of the plant samples and test methods validated. A total of four different commercially produced casting materials ranging from hypoeutectic to hypereutectic compositions were compared with an experimental high chromium white iron casting, low carbon steel and AISI 420 martensitic stainless steel.

The investigation of microstructural development involved the rigorous examination of the materials using optical and electron microscopy techniques. The chemical compositions of the alloy phases were determined using quantitative electron microprobe microanalysis. Two heat treatments at 950°C and 1150°C were done on selected casting alloys to investigate the changes in microstructure. It was found that the composition and morphology of primary and eutectic carbides were not altered as a result of heat treatment. The matrix phase was found to have more of an influence on hardness than carbide volume fraction. The experimental alloy investigated displayed a unique property such that it could not be hardened by conventional heat treatments and remained fully austenitic. The influence of cooling rate on solidification of hypereutectic compositions was found to influence the number and size of the carbides,

however, if the cooling rate was too high, undercooled carbide morphologies developed that negatively impacted on the toughness.

Corrosion tests involved potentiodynamic polarization tests in 2.5 M and 5.0 M sodium hydroxide solutions and a sodium aluminate solution representative of the early stages of the refining process at 90°C. Immersion tests on selected alloys at three different potentials were done to qualitatively investigate the effect of prolonged exposure at a particular potential. Results of the corrosion investigation found that the matrix corroded while the corrosion of the carbides was negligible. Immersion in the caustic environments resulted in the active dissolution of the matrix. Casting materials performed better than weld overlays by an order of magnitude. Mixed potential theory was used to explain the corrosion mechanism that was attributed to the galvanic interaction between the carbides and the matrix. It was found that the carbide volume fraction could not be related to corrosion performance with high carbide volume fraction alloys having superior corrosion performance to lower carbide volume fraction alloys. However, it was found that a small inter-carbide spacing, typical of the weld overlays examined, would yield a higher matrix corrosion rate. Corrosion test results strongly suggested that increasing matrix chromium composition does not improve corrosion performance of high chromium white irons in sodium aluminate solutions under freely corroding conditions, but can improve passive corrosion performance. Further work is required to absolutely define the role matrix chromium composition has on corrosion performance.

Erosion-corrosion tests involved the use of a slurry pot test apparatus and an electrochemical erosion-corrosion test apparatus that could measure in-situ corrosion behaviour. Tests were done using various size ranges and proportions of quartz particles based on alumina plant information. Erosion-corrosion of the castings was found to occur due to the erosion and corrosion of the matrix and the erosion of the carbides. Erosion-corrosion of the hypereutectic weld overlays was found to occur by the corrosion of the matrix and the erosive wear of the carbides. The movement of the solution, free of abrasive particles, over the sample surface resulted in an increased corrosion rate for both the castings and the weld overlays. The addition of erosive particles to form a slurry resulted in a further increase in the corrosion rate of the casting samples due to the synergistic interaction of erosion and corrosion. However, for the weld overlay, the slurry resulted in negligible change in corrosion rate, indicating that the synergistic interaction of erosion was not significant. The erosion of the carbides occurred due to a chipping wear mechanism at the periphery of the carbide. Larger primary carbides were found to undergo less wear than the smaller eutectic carbides. The erosive wear of the matrix for the casting samples was greater than the wear due to corrosion. The wear mechanism, irrespective of phase, was due to the platelet mechanism of erosion and consistent with this mechanism, a harder martensitic matrix resulted in less erosive wear than an austenitic matrix. For the materials investigated, the erosion-corrosion wear resistance was dependent on bulk hardness and the inter-carbide spacing.

The comparison of the wear surfaces from laboratory based erosion-corrosion tests with

ex-service plant samples showed that the laboratory wear environment resulted in a more aggressive erosive environment. However, the wear mechanisms found from the laboratory tests for both the castings and weld overlay were similar to the wear mechanisms found in the plant samples and allowed the microstructural characteristics that affect erosion-corrosion in an alumina plant environment to be determined. The laboratory results showed that erosion was the dominant wear mechanism and a material that has good erosion resistance will have good erosion-corrosion resistance. The optimum high chromium white iron would be one that has numerous closely spaced carbides, a hard martensitic matrix and sufficient strength and toughness for the intended application.

Declaration

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Publication List

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Abbreviations and Symbols

CVF - Carbide volume Fraction

EBSD - Electron back scatter diffraction

EDAX - Energy dispersive analysis of x-rays

EPMA - Electron probe microanalysis

FCAW - Flux cored arc welding

FESEM - Field emission scanning electron microscope

OCP - Open circuit potential, also known as the rest potential

PTA - Plasma transferred arc

SBL - Synthetic Bayer Liquor

SCC - Stress corrosion cracking

SCE - Standard Calomel Electrode

SEM - Scanning Electron Microscope

SHE - Standard Hydrogen Electrode

A - Ampere

mA - Milliampere

μ A - Microampere

fA - Femptoampere

E_{corr} - Open circuit potential

E_{crit} - Critical potential

E_{ref} - Potential versus reference electrode

I_{crit} - Critical current density

I_{corr} - Corrosion current density

K_{ec} - Overall erosion-corrosion rate of metal wastage

K_c - Total rate of metal wastage due to corrosion

K_e - Total rate of metal wastage due to erosion

K_{c0} - Corrosion rate in the absence of erosion

K_{e0} - Erosion rate in the absence of corrosion

ΔK_{ce} - The rate of metal wastage due to the erosion-corrosion interaction

ΔK_c - The rate of metal wastage due to the additive effect of erosion on corrosion

ΔK_e - The rate of metal wastage due to the synergistic effect of corrosion on erosion

m/s - metres per second

V - Volts

mV - millivolts

V_{RR} - Volts versus standard red rod electrode

V_{SCE} - Volts versus standard calomel electrode

V_{SHE} - Volts versus standard hydrogen electrode