A more corrosion resistant Hercules™ alloy

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Synopsis

Hercules™ is a low nickel austenitic stainless steel developed at Mintek that has a typical composition of 9 wt% Mn, 0.05 wt% C, 2 wt% Ni, 0.25 wt% N and 16.5 wt% Cr. A more corrosion resistant version of Hercules™ (Hercules™ B) with 0.5 wt% Mo has also been developed. Potentiodynamic tests performed on Hercules™ B in a 5 wt% sulphuric acid solution showed it to have improved corrosion resistance comparable to that of AISI 304. The effect of a varying Mn content on the corrosion resistance of Hercules™ B has also been investigated and the results discussed in this paper. From the corrosion test results, it is clear that decreasing the Mn content of Hercules™ B increased the corrosion rate, while increasing it decreased the corrosion rate.

Keywords: austenitic stainless steel, %ferrite, molybdenum, manganese, nitrogen, electrochemical corrosion tests, potentiodynamic scans, microstructure, chemical analysis.

Introduction

Conventional austenitic stainless steels, such as Type 304 and their low carbon grades, have good formability and weldability but they are not commonly considered for structural applications, except in instances where their corrosion resistance and toughness are required[1]. This is because austenitic stainless steels are significantly more expensive than conventional Cr-Mn structural steels due to their high nickel content of about 8 wt%. It is not necessarily the high nickel price that is a problem but rather its instability and unpredictability[2]. Hercules™ B was developed to fulfil a need for a low nickel austenitic stainless steel that would be an alternative, and not a replacement, for Cr-Mn structural steels in structural applications where high strength along with corrosion resistance and toughness at cryogenic and elevated temperatures is needed[1].

Hercules™ has higher nitrogen and lower nickel contents than conventional austenitic stainless steels such as AISI 304 and AISI 201 (Table I).

8 wt% Ni is necessary for the formation of stable austenite at room temperature, so the lowered nickel content in Hercules™ has been balanced by the addition of Mn and N, which aid in the formation and stability of austenite at room temperature. Hercules™ can attain higher strengths than conventional austenitic stainless steels (≥500 MPa) in the hot rolled and annealed conditions and has good fatigue strength and is estimated to cost 25% less than Type 304 in the hot rolled condition[2]. Hercules™, however, has lower corrosion resistance than Type-304, probably due to its lowered chromium content. Preliminary electrochemical tests showed Hercules™ to have a significantly high corrosion rate of 22-mm/y in 5 wt% sulphuric acid while AISI 304 was found to corrode at 2.8 mm/y[3]. Even though corrosion resistance is not a primary concern in the structural industry it was considered worthwhile to develop a more corrosion resistant Hercules™ alloy (Hercules™ B) that could find applications where corrosion resistance is mandatory[4].

The addition of molybdenum to improve the corrosion resistance of austenitic stainless steels is a common practice such as in the Type 316 austenitic stainless steels. An addition of 0.5 wt% Mo was sufficient to improve the corrosion resistance of Hercules™ in 5 wt% sulphuric acid and 3.56 wt% NaCl to values comparable to those of Type 304 steels by lowering the critical and passive current densities and also increasing the pitting potential[4].

Manganese aids nitrogen solubility and is almost always used in conjunction with this element. Manganese is generally deemed to

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Table I

Base composition of the Hercules™ alloy

Alloy	C	Si	Mn	Cr	Ni	N
Hercules™	0.05	0.50	9.0	16.5	2.00	0.25
AISI 304	0.04	0.50	1.5	18.3	8.50	0.05
AISI 201	0.10	0.50	6.5	17.0	5.0	0.15

have a negative effect on the corrosion rate of stainless steel and has also been found to weaken the passive film and decrease the protectiveness of the film[5]. Manganese can also be detrimental to the pitting resistance of austenitic stainless steels if the formation of manganese sulphide inclusions, which are favourable sites for pit initiation, occurs[6].

It is the aim of this paper to determine the effect of variations in the manganese content on the corrosion resistance of the more corrosion resistant Hercules™ B alloy. The alloy was tested using electrochemical methods and trends in the corrosion rate with a varying Mn content noted.

Experimental procedure

Alloy production and chemistry

Five kg ingots were manufactured in a vacuum furnace in an argon atmosphere with the aim of producing three Hercules™ B base composition alloys with varying manganese contents (referred to as HB 1, HB 2 and HB 3 in Table II). The ingots were homogenized at 1200°C for 4 hours and then hot rolled at 1050°C from 40 mm to 20 mm plates and water quenched. The plates were then annealed at 1100°C for 2 hours and air cooled so that any segregation or tension built up during quenching could be eliminated. The composition of the hot rolled and annealed alloys was analysed by spark emission spectrometry and nitrogen by a LECO method.

Microstructural analysis

Cross-sections were cut transverse to the rolling direction of the three alloys. These were mounted, ground, polished and etched to study the microstructure. 10% oxalic acid at 2.5 V for 6 seconds was used to reveal austenite and 75% potassium hydroxide (KOH) at 6V for 90 seconds to reveal delta-ferrite.

Corrosion measurements

General corrosion

All the alloys were tested for general corrosion behaviour according to ASTM standard G5–94 (2002) in a 5 wt% sulphuric acid solution, at 30°C. The solution was purged with nitrogen for an hour prior to and during scanning. The alloys were ground to a 600-grit surface finish before testing. A three-electrode corrosion cell with carbon as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode was used. The scan was started at –200 mV vs. E_{corr} and ended at 1200 mV at a rate of 10 mV/min. Duplicate scans were performed per alloy. Figure 1 is an example of a typical scan obtained during testing, showing reproducible results.

General corrosion rate calculation

The corrosion current density (i_{corr}) was calculated directly from the potentiodynamic scans by determining the polarization resistance (R_p) of each alloy from the scans. Polarization resistance is defined as the slope of the voltage-current density scan in the range ±30 mV from E_{corr}[7]. This range is not restricted to 30 mV, but can be as small as 15 mV or even 10 mV from E_{corr}. Drawing the above mentioned range on a linear scale and then calculating the slope at the origin yielded R_p as shown in Figure 2.

From Figure 2 the slope and hence R_p is 20.698 Ω. cm² and i_{corr} can be found using Equation [1][7].

$$R_p = \frac{B}{i_{corr}} \quad \textbf{where} \quad B = \frac{\beta_a \times \beta_c}{2.3(\beta_a + \beta_c)} \qquad [1]$$

Subscripts *a* and *c* stand for anodic and cathodic, respectively, while *ßa* and *ßc* are Tafel slopes and *ßa*=*ßc* = 0.1 was used as is explained in Jones[6].

Results and discussion

Chemistry

The compositions of the alloys made (HB 1, HB 2 and HB 3 in Table II) were within the Hercules™ B base composition

Table II

Composition of the 5 kg ingots

Alloy	Elements						
	C	Si	Ni	Cr	Mo	N	Mn
*304	0.04	0.50	8.5	18.3	-	0.05	1.50
*201	0.1	0.5	5.0	17.0	-	0.15	6.50
Herc™ B	0.027	0.45	2.10	15.9	0.52	0.14	9.33
HB 1	0.036	0.36	2.19	15.4	0.44	0.12	5.02
HB 2	0.031	0.49	2.22	15.6	0.45	0.17	4.91
HB 3	0.029	0.50	2.23	15.9	0.46	0.25	15.40

* Typical compositions of the reference alloys

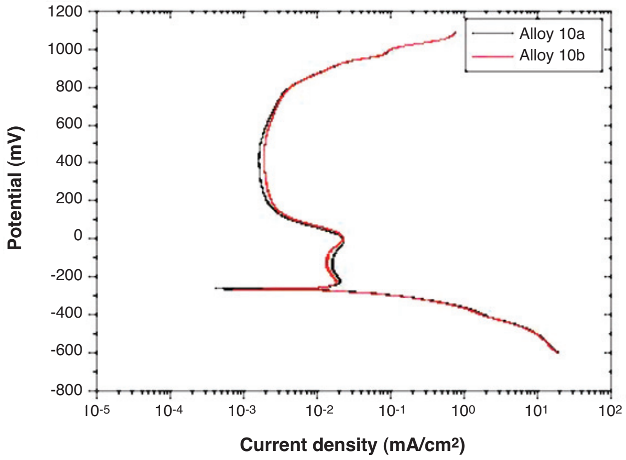

Figure 1—Typical potentiodynamic scan obtained for the alloys in 5 wt% sulphuric acid

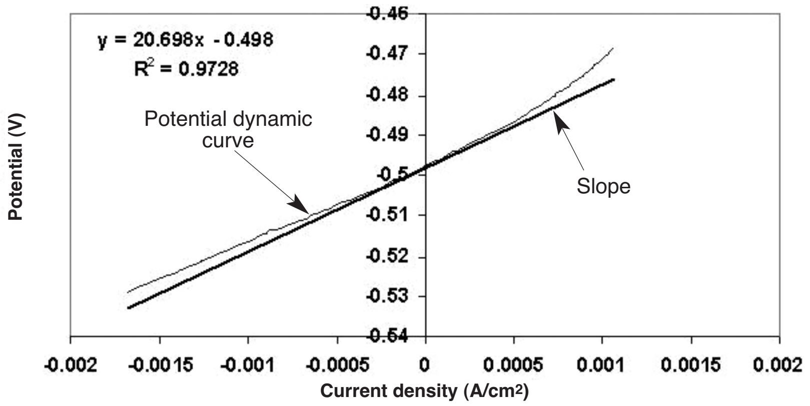

Figure 2—Part of the potentiodynamic scan drawn ±15 mV from E_{corr} and the slope

Table III

Microstructures of tested alloys

Alloy	10% Oxalic acid	75% Potassium hydroxide	% Ferrite
Hercules™ B	Consists of coarse austenite structure (Figure 3a)	Shows a low percentage of delta ferrite (Figure 3b)	0.38
HB 1	Consists of austenite and martensite (Figure 4a)	Shows low percentage of delta ferrite (Figure 4b)	6.8
HB 2	Austenite (Figure 5)	No ferrite was detected	0
HB 3	Consists of coarse austenite structure (Figure 6)	No ferrite was detected	0

*In all accompanying figures α' = martensite, γ = austenite, ∝ = delta-ferrite

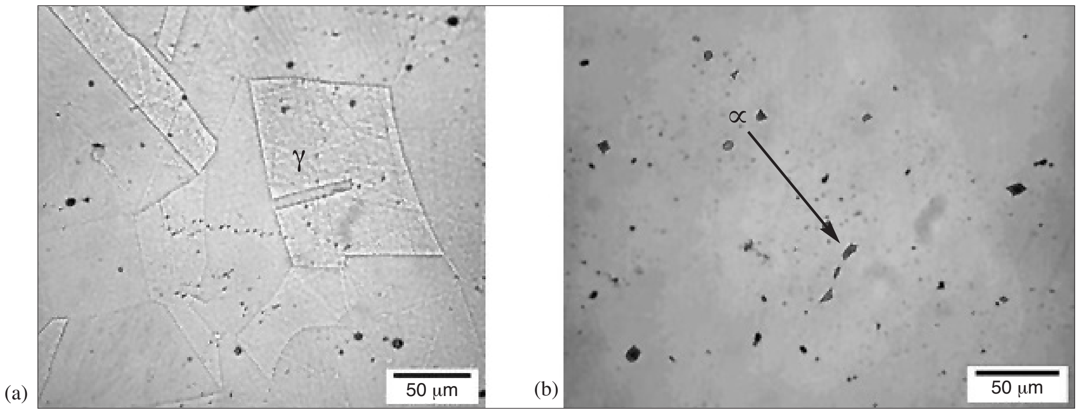

Figure 3—Microstructure of Hercules™B as revealed by 10% oxalic acid (a) and 75% potassium hydroxide (b)

except for nitrogen, which was lower than targeted in all cases except for alloy HB 3. Nitrogen is difficult to keep in solution at high melting temperatures because its solubility decreases as the temperature increases. Despite variations in nitrogen content, the alloys were still compared to determine the effect of manganese on the corrosion resistance of Hercules™ B. Manganese was increased form 5.02 wt% to 15.4 wt%. Reference alloys used were AISI 304 and 201.

Microstructures of the manufactured alloys

Table III lists the microstructures obtained for the alloys made. The %ferrite was measured with a Feriscope® MP30 ferritescope, which measures magnetism and can thus detect the quantity of martensite or ferrite phases in an alloy since these are magnetic phases.

It is evident that as manganese increases in the base alloys the delta-ferrite content decreases (Table III). This is to be expected because manganese is an austenite former and stabilizer that hinders the formation of delta-ferrite in the microstructure[8]. Manganese also aids nitrogen solubility, which again aids in the formation of stable austenite at room temperature[5,8].

The microstructures of the alloys do not differ significantly from that of Hercules™ B since they are all composed of austenite and some ferrite, except for alloy 1 which had some martensite (see Figure 4a).

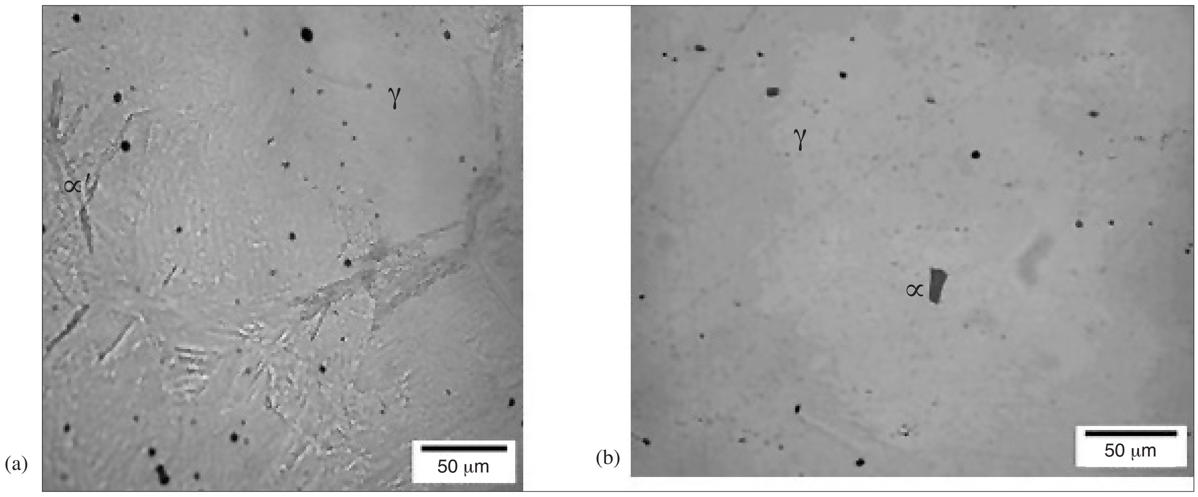

Figure 4—Microstructure of alloy 1 as revealed by 10% oxalic acid (a)

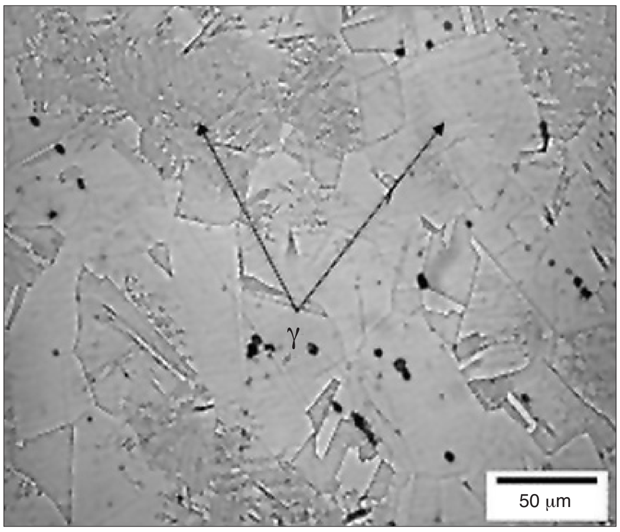

Figure 5—Microstructure of alloy 2 as revealed by 10% oxalic acid and 75% potassium hydroxide

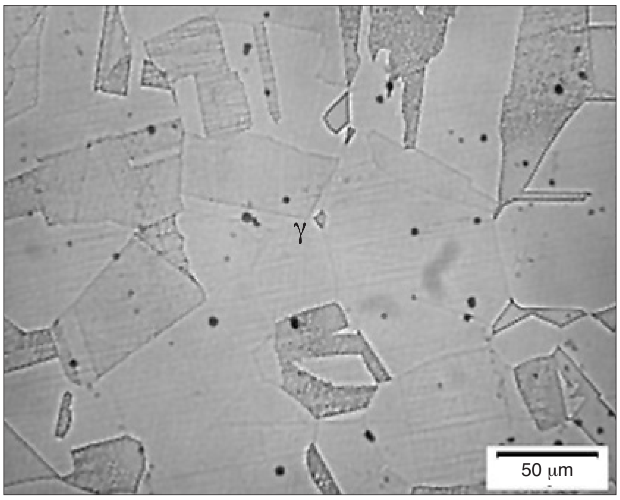

Figure 6—Microstructure of alloy 3 as revealed by 10% oxalic acid

General corrosion

Table IV lists the corrosion rate (mm/y) of the alloys made along with the three reference alloys. i_{pass} and i_{crit} values are also listed in Table IV and these results are graphically represented in Figure 7.

The Hercules™ B alloy was determined to have a corrosion rate of 0.29 mm/y, which is much lower than that of the original Hercules™ alloy (22 mm/y). Corrosion rates of alloys HB 1 and HB 2 with about 5 wt% Mn are higher than those of Hercules™B and those at 15 wt% are lower. It seems then that an increase in manganese improves the corrosion rate of Hercules™ B alloy and a decrease in manganese content, reduces its corrosion resistance. Varying the manganese content of the alloys did not have much effect on ther i_{pass}. and i_{crit} of the alloys improved with an increasing Mn content, suggesting that manganese improves corrosion resistance by allowing for easier passivation.

Figure 7 is a graphical representation of the results in Table III and it shows that at 5 wt% Mn the alloys have a corrosion rate similar to AISI 201 and at 15 wt% Mn the alloys have a corrosion rate lower than Hercules™ B and AISI 304. A composition of 10 wt% Mn is optimum for the Hercules™ B alloy since the Mo addition at this manganese level of the alloy is sufficient to lower the corrosion rate to values comparable to that of AISI 304.

Conclusions

The following conclusions can be drawn form the results

- A decrease in manganese of Hercules™ B to 5wt%, increases its corrosion rate significantly to values comparable to AISI 201.
- An increase in manganese of Hercules™ B to 15 wt%, decreases its corrosion rate even further to values even better than AISI 304.
- 10 wt% Mn is optimum since molybdenum lowers the corrosion rate sufficiently to levels comparable to AISI 304.

Table IV

Corrosion rate of tested alloys

Alloy	Wt% Mn	Wt% N	Corrosion rate (mm/year)	i_{pass} (A/m^2)	i_{crit} (A/m^2)
304	1.50	0.05	0.48	0.043	0.250
201	6.50	0.15	7.83	0.015	0.010
Herc™ B	9.33	0.14	0.29	0.017	0.140
HB 1	5.02	0.12	9.47	0.011	4.450
HB 2	4.91	0.17	11.61	0.010	5.960
HB 3	15.4	0.25	0.10	0.010	0.060

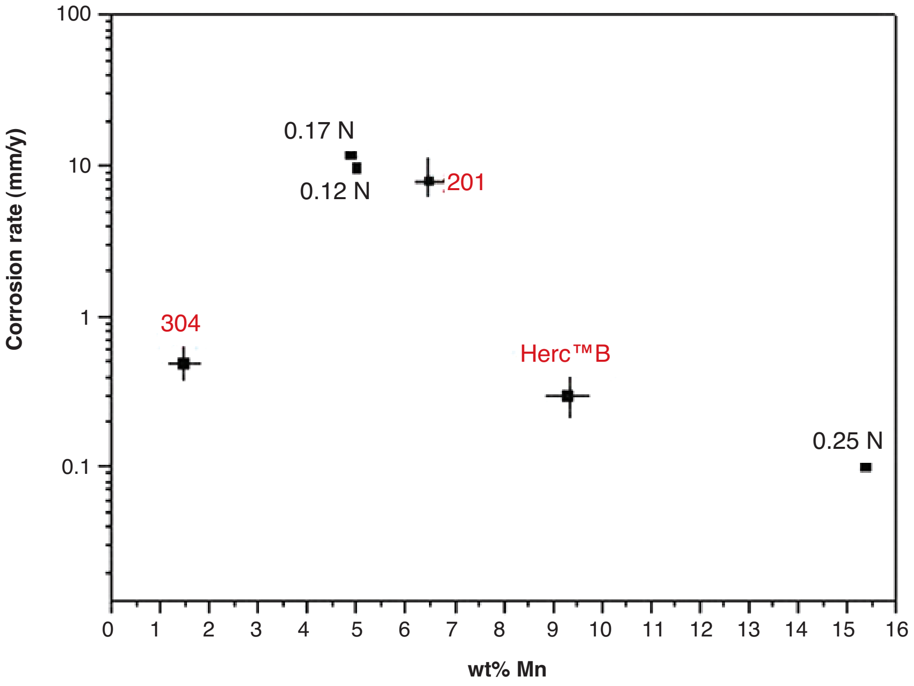

Figure 7—The effect of manganese on the corrosion rate of Hercules™B

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