

# Microstructure and corrosion resistance of experimental low-nickel duplex stainless steels

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## SYNOPSIS

Duplex stainless steels containing high levels of manganese and copper and lower-than-normal levels of nickel were produced and evaluated. The experimental alloys containing 3 per cent copper by mass could not be successfully hot-rolled. Alloys containing less than 2 per cent copper could be hot- and cold-rolled without difficulty.

The wrought experimental alloys that contained copper were found to offer some advantages over the 2205-type duplex stainless steel in sulphuric acid at 52°C. Resistance to pitting attack was governed primarily by the chromium, molybdenum, and nitrogen contents, and one of the experimental alloys was superior to the 2205-type alloy in the ferric chloride test.

It is concluded that manganese is a useful substitute for nickel in duplex alloys, but that further work is required before the present alloys, or variations of them, could be commercially viable.

## SAMEVATTING

Dupleksvlekvryestaal met hoë vlakke van mangaan en koper en nikkelvlaeke wat laer as normaal is, is geproduseer en geëvalueer. Die eksperimentele legerings wat 3 massapersent koper bevat, kon nie suksesvol warmgewals word nie. Legerings met minder as 2 persent koper kon sonder probleme warm- en koudgewals word.

Die eksperimentele smeelegerings met koper het in swaelsuur by 52°C sekere voordele vergeleke met die dupleksvlekvryestaal, tipe 2205, gehad. Bestandheid teen invreting is in die eerste plek deur die chroom-, molybdeen- en stikstofinhoud bepaal, en een van die eksperimentele legerings was beter as die tipe 2205-legering in die ferrichloried.

Die gevolgtrekking is dat mangaan 'n nuttige plaasvervanger vir nikkel in duplekslegerings is, maar dat daar nog werk gedoen sal moet word voordat huidige legerings, of variasies daarvan, kommersieel lewensvatbaar kan wees.

## INTRODUCTION

Stainless steels consisting of at least 20 per cent ferrite and 20 per cent austenite are termed duplex stainless steels. Forerunners to the modern duplex stainless steels appeared<sup>1,2</sup> in the 1930s, but duplex stainless steels did not gain much market share until the 1970s. Duplex stainless steels combine the good resistance of ferritic steels against stress-corrosion cracking with the good ductility of austenitic steels. Furthermore, the duplex structure induces a yield strength that is about twice that of austenitic steels. The thermal expansion and thermal conductivity coefficients are intermediate between those of ferritic and austenitic stainless steels. With only about half or less of the nickel content of the common austenitic alloys, they are less sensitive to the nickel price<sup>3,4</sup>.

The key to the success of duplex stainless steel may have been the introduction of nitrogen into their compositions<sup>2</sup>, as well as their use in equipment in the North Sea oilfields<sup>1</sup>. Examples<sup>5</sup> of duplex stainless steels available in the late 1970s were type 329, AL 326, and Sandvik's 3RE60. These alloys contained less than 0,02 per cent nitrogen by mass, and normally contained a ferritic heat-affected zone (HAZ) after welding. As a result, it was frequently necessary to

solution anneal after welding in order to obtain the desirable duplex microstructure. In contrast, modern or second-generation duplex stainless steels have a nitrogen content of 0,15 per cent or more. Nitrogen is a potent austenite former, since it moves the  $\gamma/\alpha$  phase boundary to higher chromium contents and higher temperatures. The latter factor ensures that the HAZ of weldments in nitrogen-bearing duplex stainless steels contain balanced quantities of austenite and ferrite in the as-welded condition<sup>4,6</sup>. Nitrogen also reduces the partitioning of alloy elements between the austenite and the ferrite phase<sup>7,8</sup>, and is known to improve pitting resistance<sup>1,6</sup>.

Table I lists a few of the duplex compositions that are currently manufactured. The compositions throughout this paper are given in percentages by mass.

**Table I**  
Nominal compositions of some commercially available duplex stainless steels in percentages by mass

Alloy	Cr	Ni	Mo	C	Other elements*
AISI 329	28,0	6,0	1,5	0,10	2 Mn, 1 Si
AL 326	26,0	6,5	0	0,05	0,25 Ti
3RE60	18,5	4,5	2,5	0,02	1,5 Mn, 1,6 Si
SAF 2205	22,0	5,5	3,0	0,02	0,15 N
Ferralium 255	25,5	5,5	3,0	<0,04	2 Cu, 0,18 N
Zeron 100	25,0	7,0	3,5	<0,03	0,8 Cu, 0,8 W, 0,25 N
Uranus 52N	25,0	6,5	3,0	<0,03	0,17 N, 1,5 Cu

\* Elements not mentioned are present in their typical concentrations

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While duplex stainless steels contain less nickel than most austenitic stainless steels, they normally have a nickel content of at least 4 per cent. The comparatively high price of nickel ensures that nickel is responsible for a significant portion of the price of duplex stainless steel. However, while nickel is a convenient austenite-forming element, it is not the only one. Manganese, copper, and nitrogen are examples of other elements that have some austenite-forming ability. This paper describes a series of experimental duplex stainless steels in which part of the nickel content was replaced with manganese, nitrogen, and copper. Two types of alloy were studied: alloys containing 22 per cent chromium, designed to replace the generic 2205-type duplex stainless steel; and three lean duplex stainless steels containing less than 20 per cent chromium, designed to be equivalent to the proprietary duplex stainless steel 3RE60.

## EXPERIMENTAL

### Alloy Manufacture

The alloys, made up of appropriate mixtures of the elements and ferro-alloys, were melted in a vacuum-induction furnace under a partial pressure of argon. The compositions of the alloys containing 22 per cent chromium are listed in Table II, while Table III shows the compositions of the three lean duplex stainless steels. After casting, the alloys were soaked at an elevated temperature, and were then forged from 50 mm to 45 mm before being hot-rolled, with reheating, to 6 mm plate. Alloy X2 broke up during rolling and could not be produced as plate. Additional details of the reduction process are given in Table IV.

### Metallography

The percentage of ferrite in the experimental alloys was estimated by computerized image analysis (IA) using a Leica Quantimet 520 Image Analyzer. Electrolytic etching in 40 per cent KOH solution was found to be suitable for the wrought alloys. This treatment coloured the ferrite brown. However, the cast alloys did not respond sufficiently to this etchant, and were etched with one of Beraha's tint etchants. Further details of the composition

**Table II**

Experimental duplex stainless steels containing 22 per cent chromium

Alloy	Melt	C	Si	Mn	Cr	Ni	Mo	Cu	N
X0	VF599	0,029	0,60	0,93	21,6	5,07	2,94	0,02	0,14
X2	VF604	0,045	0,46	4,41	21,8	2,20	3,05	3,02	0,14
X3	VF642	0,039	0,60	6,40	21,7	2,70	2,45	3,40	0,19
X4	VF643	0,045	0,50	6,68	22,3	2,70	2,40	3,06	0,27
X5	VF656	0,014	0,46	6,25	22,4	2,65	2,55	0,04	0,37
X6	VF655	0,025	0,45	5,52	21,6	3,10	2,91	1,42	0,28
X7	VF739	0,043	0,54	6,91	22,0	2,38	1,04	0,75	0,24

**Table III**

Experimental duplex stainless steels containing 19 per cent chromium

Alloy	Melt	C	Si	Mn	Cr	Ni	Mo	Cu	N
C4	VF906	0,035	0,30	6,60	19,6	2,10	0,02	3,05	0,09
X1	VF602	0,037	0,55	4,63	19,2	2,10	2,20	3,20	0,09
M11	VF720	0,045	0,42	6,87	18,7	3,88	0,04	0,54	0,09

**Table IV**  
Hot-rolling parameters

Alloy	Soaking temperature, °C	Passes before reheating
X0	1150	4 x 1 mm
X1	1150	4 x 1 mm
X2	1150	4 x 1 mm
X3	1060	2 x 2 mm
X4	1060	2 x 2 mm
X5	1050	3 x 2 mm
X6	1050	3 x 2 mm
X7	1050	3 x 2 mm
C4	1050	Varied
M11	1050	Varied

and etching conditions for both etchants are given in Table V. Fifty fields were analysed on each sample, and the standard error was approximated by the standard deviation of the measurements. One of the specimens, M11, was subjected to both Beraha's reagent and potentiostatic etching in KOH so that the IA results for the two etchants could be compared. X-ray diffraction (XRD) analysis was also applied to this specimen, and gave essentially the same result as image analysis. Additional experimental details, as well as a discussion of the merits of IA versus XRD in duplex stainless steels, are given elsewhere<sup>9</sup>.

Although the Beraha etchant used usually darkens the

**Table V**  
Etchants and conditions used to differentiate ferrite from austenite in the present work

Etchant	Composition	Conditions
KOH	45 g KOH, 60 ml H <sub>2</sub> O	2,5 V for 5 to 10 s
Beraha's-I	100 ml stock, 1 g K <sub>2</sub> S <sub>2</sub> O <sub>5</sub>	Wet etch, immersed until surface changed colour

austenite phase in austenitic stainless steels, it normally tints the ferrite phase in duplex stainless steels, a point mentioned by Vander Voort<sup>10</sup>. However, it was found in the present alloys that the etchant attacked the ferrite even in the M11 alloy, which, as will be seen later, was substantially austenitic. The application of the identical etching conditions to a sample of type 304 weld metal that contained 12 per cent  $\delta$ -ferrite, on the other hand, caused staining of the austenite phase, as expected from the literature. Consequently, it is concluded that Beraha-I may tint either austenite or  $\delta$ -ferrite, even in substantially austenitic stainless steels.

## Corrosion Testing

### Mass-loss Tests

The rate of corrosion in sulphuric acid was determined substantially in accordance with ASTM Standard G31<sup>11</sup>. Test coupons were cut from the cold-rolled sheet, ground with 800 grit emery paper, sand-blasted, degreased ultrasonically, rinsed in de-ionized water followed by alcohol, and air-dried. The dimensions of the coupons were measured so that the total area of interest could be calculated. After the coupons had been weighed to the nearest 0,001g, they were placed in sulphuric acid at concentrations of from 10 to 50

per cent by volume. A reflux condenser with an atmospheric seal was used to minimize evaporation losses. The solutions were held at 52°C using a thermoregulator, and they were agitated with a magnetic stirrer.

After the test, the coupons were scrubbed with a bristle brush and a mild abrasive, and were then cleaned ultrasonically. This process was repeated twice, followed by rinsing in water and a suitable solvent, and drying in air. The mass lost during the test period was used as the principal measure of corrosion. Corrosion tests in 30 per cent acid and acid of lower concentration by volume were conducted in triplicate while, at acid concentrations of 40 per cent and higher, the testing was in quintuplicate.

### Pitting Tests

Pitting-corrosion tests were conducted in accordance with ASTM G48 Method A, Total Immersion Ferric Chloride Test<sup>12</sup>. The test coupons were prepared in triplicate, in the same way as those for the sulphuric acid testing, and were then exposed in 10 per cent FeCl<sub>3</sub>·6H<sub>2</sub>O solution for 4 hours at 40°C and 52°C, and for 12 hours at ambient temperature (about 22°C). The specimens were mounted on glass cradles. After exposure, the specimens were rinsed in water, scrubbed with a nylon bristle brush under running water to remove corrosion products, ultrasonically cleaned and dried using methanol, and weighed to 0,001 g.

## RESULTS

### Hot and Cold Workability

The base composition X0 could be hot-rolled without difficulty, but all the alloys containing 3 per cent copper developed cracks at their edges during hot-rolling. However, the alloys containing less than 1,5 per cent copper (X5, X6, X7, and M11) could be hot-rolled to 6 mm plate without cracking. Figure 1 shows the 'alligator' fracture obtained when an attempt was made to hot-roll X2, which contained 3 per cent copper. Figure 2 compares the appearance of the 75 mm wide plates rolled from X0 (no copper) and X1 (3 per cent copper). The superior hot-workability of the X0 composition is quite apparent. An examination of the microstructures indicated that the cracks followed the austenite–ferrite grain boundaries (Figure 3).

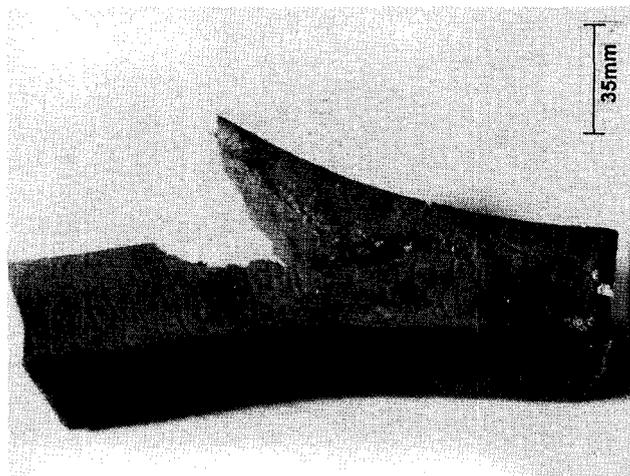


Figure 1—Severe hot cracking resulting from an attempt to hot-work experimental alloy X2

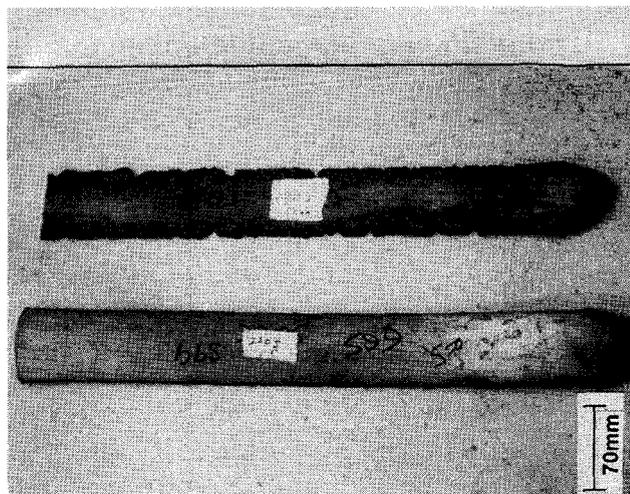


Figure 2—A comparison of hot-rolled plate manufactured from the X0 and X1 experimental alloys

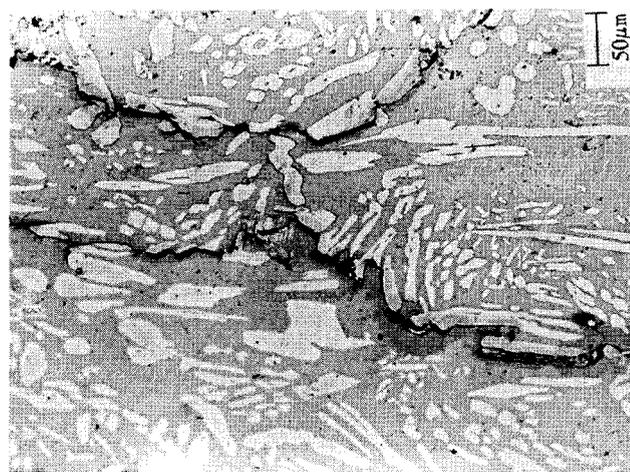


Figure 3—Microstructure of partially hot-worked ingot alloy X2, showing cracks between the ferrite (dark) and the austenite (light) phases

Alloys X0, X5, X6, X7, M11, and C4 were subsequently cold-rolled to sheet of between 1 and 2,5 mm thickness without any further difficulty.

### Microstructure

The percentage ferrite in the microstructures of the various alloys after solution heat-treatment at 1050°C is given in Table VI. Also listed are the chromium and nickel equivalents of the various alloys calculated from the following formulae<sup>5</sup>:

$$Cr_{eq} = Cr + 1,5 Mo + 2 Si$$

and

$$Ni_{eq} = Ni + 0,5 Mn + 0,3 Cu + 30 C + 25 N.$$

The X0 alloy was intended as a laboratory-produced equivalent to the generic 2205-type alloy, but turned out to be somewhat leaner in austenite-forming elements than the commercial alloy. This is reflected in its significantly higher ferrite volume fraction. (Commercial heats of the 2205-type alloys would be expected to contain from 40 to 50 per cent ferrite<sup>2,13</sup> after quenching from 1050°C.)

**Table VI**  
**Microstructures after solution heat-treating at 1050°C**  
**for 30 minutes and water quenching**

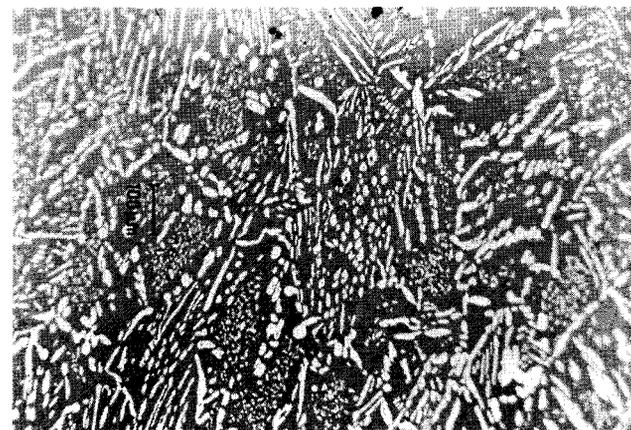
Alloy	Condition	Ferrite, %	Method	N <sub>req</sub>	Cr <sub>eq</sub>
X0	Wrought	61,0 ± 5,5	KOH	9,9	27,2
X1	Cast	58,1 ± 9,7	B-I	8,7	23,6
X2	Cast	65,1 ± 7,7	B-I	10,2	27,3
X3	Cast	57,6 ± 6,0	B-I	12,8	26,6
X4	Cast	52,7 ± 7,7	B-I	15,1	26,9
X5	Wrought	55,4 ± 6,0	KOH	15,5	27,1
X6	Wrought	60,9 ± 4,3	KOH	14,0	26,9
X7	Wrought	49,0 ± 5,0	KOH	13,4	24,6
C4	Wrought	52,0 ± 6,0	KOH	9,6	20,2
M11	Wrought	14,1 ± 3,6	KOH	11,1	19,6
M11	-	13,2 ± 2,8	B-I	-	-
M11	-	16,4 ± 3	XRD	-	-

The as-cast alloys consisted of a ferrite matrix containing a dispersion of Widmanstätten austenite. Figures 4 to 7 compare the microstructures of the alloys that could not be successfully hot-worked, after a solution heat-treatment at 1050°C followed by quenching in water. Alloy X1 (containing 19 per cent chromium) consisted of sharply-pointed Widmanstätten austenite in a matrix of δ-ferrite (Figure 4). Alloy X2, which contained 22 per cent chromium and only 2 per cent nickel, also consisted of austenite in ferrite, but the austenite was more equi-axed and rounded, suggesting that the transformation of the original δ-ferrite to austenite had occurred at a higher temperature than in X1 after the ingot solidified (Figure 5). Alloys X3 and X4, which were nominally of the Fe-22 Cr-6,5 Mn-3 Ni-3 Cu-2,5 Mo-0,22 N type, consisted of acicular austenite in ferrite, with a character in between that of X1 and X2 (Figures 6 and 7).

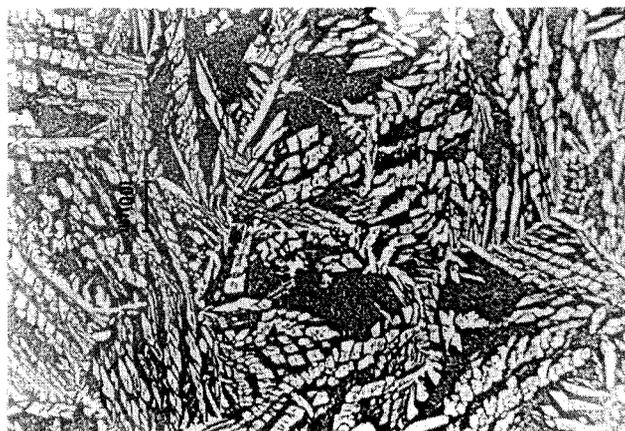
The X2 alloy contained only 2 per cent nickel, compared with 5 per cent nickel in the base alloy X0, and it is evident from Table VI that the substitution of 4 per cent manganese and 3 per cent copper for the missing 3 per cent nickel was not quite adequate, notwithstanding the similar chromium and nickel equivalents of the two alloys. The X3 and X4 alloys were developed from X0 by the elimination of 2 per cent nickel and 1 per cent molybdenum from the latter composition, and the substitution of 5 per cent manganese, 3 per cent copper, and an additional 0,1 per cent nitrogen. The X3 variation is lean in austenite-forming elements, whereas X4



**Figure 4—Microstructure of cast alloy X1 after quenching from 1050°C. Widmanstätten austenite (light) in ferrite plus austenite matrix**



**Figure 5—Microstructure of cast alloy X2 after quenching from 1050°C. Austenite (light) in ferrite matrix**



**Figure 6—Microstructure of cast alloy X3 after quenching from 1050°C. Needles of austenite (light) in ferrite plus austenite matrix**



**Figure 7—Microstructure of cast alloy X4 after quenching from 1050°C. Needles of austenite (light) in ferrite plus austenite matrix**

is significantly richer. The difference between the two alloys, as well as the effect of temperature on their constitution, can be seen in Figure 8. It is evident that the larger nickel equivalent of X4 has resulted in less ferrite being present in the microstructure.

The microstructures of alloys X1 to X4 indicate that they solidified as δ-ferrite, and subsequently precipitated austen-

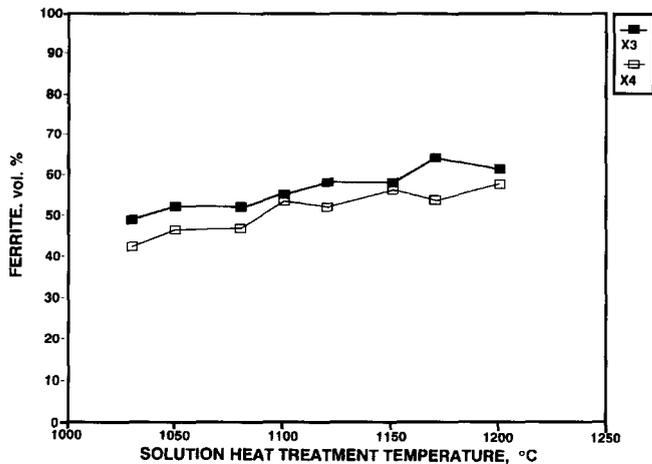


Figure 8—Effect of temperature on the constitution of experimental alloys X3 and X4

ite as they cooled. Lippold and Savage (cited in Solomon and Devine<sup>2</sup>) term these kinds of alloys 'Zone 4 hyper-pseudo-eutectic alloys', and note that they are immune to solidification cracking, unlike hypo-pseudo-eutectic alloys (which solidify first as austenite).

The wrought alloys X5 and X6 differed slightly in composition, but had similar chromium equivalents. The higher nickel equivalent of X5 compared with X6 was reflected in the microstructure, and X5 contained about 5 per cent more austenite than X6. However, alloy X7, which had lower nickel and chromium equivalents than X6, actually contained 10 per cent more austenite. Alloy X7 contained only 1 per cent molybdenum, compared with the 3 per cent in X6, and the greater amount of austenite may be because the formulae for austenite and chromium equivalents are only first-order, linear approximations of the real situation. The microstructures of these alloys are shown in Figures 9 to 11, and are similar to the microstructures of commercial wrought duplex alloys.

The lean duplex alloy X1, which contained only 19 per cent chromium and had lower nickel and chromium equivalents than X0, consisted of 58 per cent ferrite, similar to alloy X0. Alloy M11 contained significantly more nickel and manganese than X1, and also contained no molybdenum. The result was a substantially austenitic alloy (Figure 12). The other lean duplex composition, C4, contained

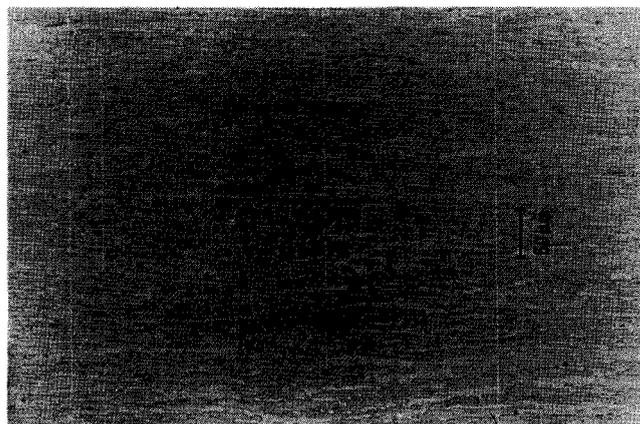


Figure 9—Microstructure of cold-rolled alloy X5 after quenching from 1050°C. The continuous phase is austenite

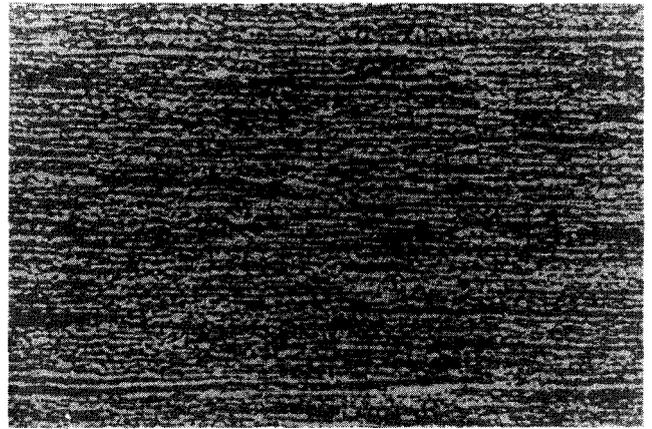


Figure 10—Microstructure of cold-rolled alloy X6 after quenching from 1050°C

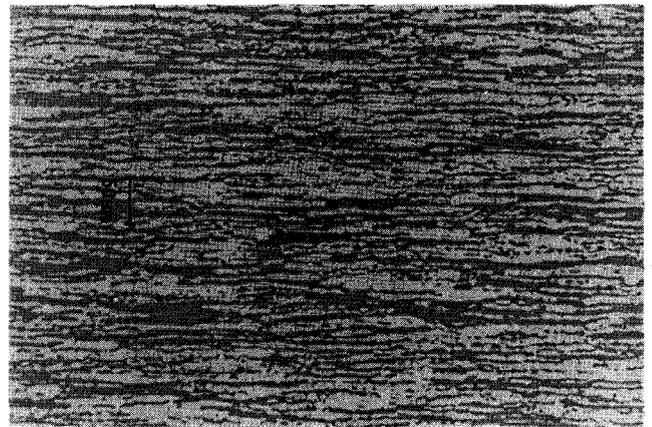


Figure 11—Microstructure of cold-rolled alloy X7 after quenching from 1050°C

about 40 per cent more ferrite than M11, but differed in composition mainly in that it contained 2 per cent less nickel and 2,5 per cent more copper (Figure 13), clearly indicating that copper is a poorer austenite former than nickel.

### Corrosion Resistance

The most promising of the experimental alloys were selected for corrosion testing. The 19 per cent chromium

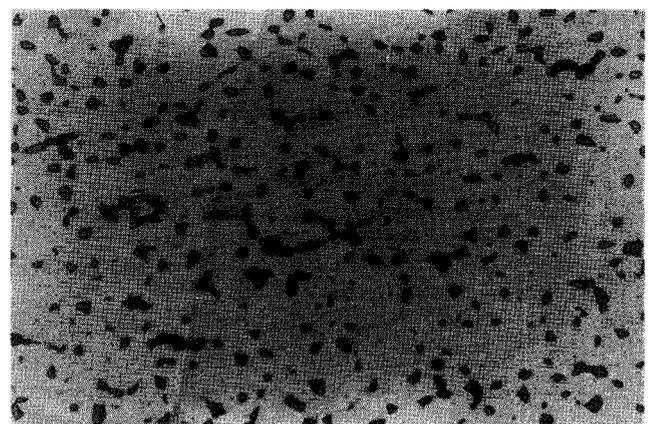


Figure 12—Microstructure of cold-rolled alloy M11 after quenching from 1050°C. The alloy is substantially austenitic

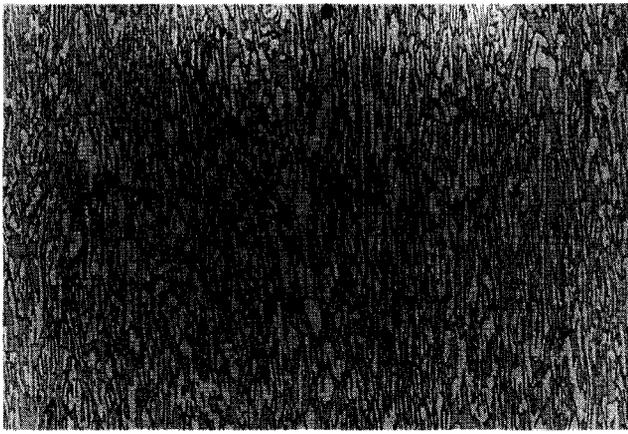


Figure 13—Duplex microstructure of hot-rolled wrought alloy C4 after quenching from 1050°C

alloys and the alloys that could not be successfully hot-worked were not tested.

### Sulphuric Acid

The results of mass-loss tests in sulphuric acid on alloys X0, X5, X6, and X7 at 55°C are given in Table VII and in Figure 14. If 0,1 mm/y is taken as the maximum rate of corrosion that can be accepted by a user, it is evident that alloys X5 to X7 are superior to the base alloy, X0, since they are much more resistant to corrosion at concentrations of up to 20 per cent H<sub>2</sub>SO<sub>4</sub>. The X0 alloy was resistant up to only about 10 per cent H<sub>2</sub>SO<sub>4</sub> at that temperature. However, isocorrosion charts<sup>13</sup> for the corrosion of commercial SAF2205 in sulphuric acid indicate that this alloy should corrode at less than 0,1 mm/y at 55°C for acid concentrations of less than 25 per cent. It therefore appears that the corrosion resistance of the base alloy X0 in sulphuric acid was affected deleteriously by its excess ferrite content.

The alloys with the best overall corrosion resistance at 55°C in 10 to 20 per cent H<sub>2</sub>SO<sub>4</sub> are the copper-containing alloys X6 and X7. The lean duplex X7 continues to be a good option in solutions somewhat in excess of 40 per cent H<sub>2</sub>SO<sub>4</sub>, and exhibits a corrosion rate of no more than 0,4 mm/y in that range. None of the alloys tested is suitable in higher concentrations of acid at that temperature. The alloy with 3 per cent nickel and no copper, X5, had the worst corrosion resistance overall.

### Ferric Chloride

The results of the pitting tests in ferric chloride are given in Table VIII and Figure 15. It is apparent that the lean duplex alloy, X7, had the worst resistance to pitting attack,

Table VII

Rate of corrosion, mm/y, of 22 per cent chromium wrought experimental alloys in sulphuric acid at 52°C

Alloy	Acid concentration, % by volume				
	10	20	30	40	50
X0	0,07 ± 0,02	0,58 ± 0,07	0,61 ± 0,08	21,7 ± 1,7	356 ± 20,1
X5	0,11 ± 0,01	0,12 ± 0,05	0,82 ± 0,04	690 ± 39	789 ± 10,4
X6	0,01 ± 0,04	0,10 ± 0,08	2,67 ± 0,10	20,2 ± 0,87	88 ± 4,7
X7	0,02 ± 0,03	0,07 ± 0,01	0,22 ± 0,09	0,34 ± 0,03	856 ± 346

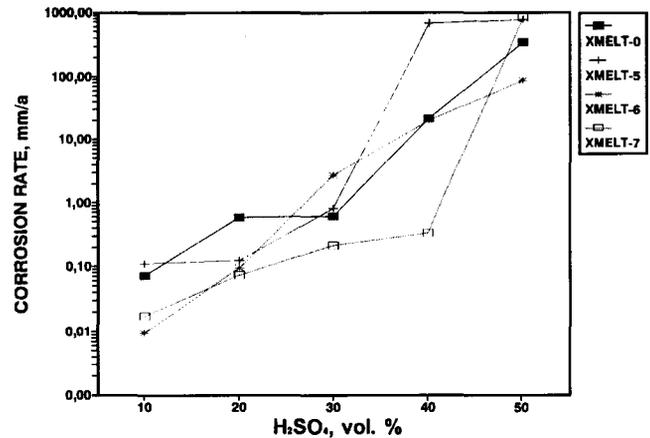


Figure 14—Corrosion of selected experimental alloys in sulphuric acid at 52°C

Table VIII

Rate of corrosion, mm/y, of 22 per cent chromium wrought experimental alloys in 10 % FeCl<sub>3</sub> at various temperatures

Alloy	PRE number	Mass loss, mm/y		
		22°C	40°C	52°C
X0	34	0,10 ± 0,01	1,71 ± 0,43	8,37 ± 0,28
X5	38	0,09 ± 0,01	0,33 ± 0,01	4,21 ± 0,26
X6	38	0,18 ± 0,02	0,23 ± 0,16	6,22 ± 0,21
X7	29	6,67 ± 0,88	15,9 ± 0,78	57,5 ± 0,43

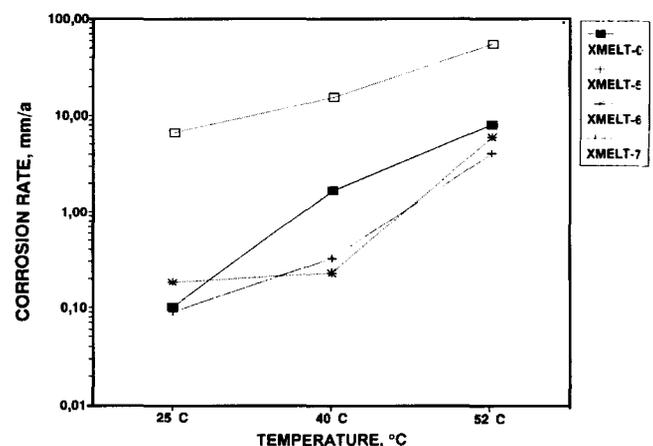


Figure 15—Rate of corrosion of wrought 22 per cent chromium alloys in FeCl<sub>3</sub> solutions held at various temperatures

followed by alloy X0. The pitting resistance equivalents (PRE) for these alloys were calculated from the formula<sup>1</sup>

$$PRE = (\%Cr) + 3,3(\%Mo) + 16(\%N),$$

and are also given in Table VIII. It is evident that pitting-corrosion resistance was significantly higher for the alloys with higher PREs. The PRE is frequently used as a guide to pitting- and crevice-corrosion resistance. For example, it is generally considered that PREs higher than 35 are necessary to ensure that an alloy will display good pitting performance in seawater<sup>1</sup>.

The poor performance of alloy X7 was due to the fact that it contains less molybdenum and nitrogen than the other alloys. Alloys X5 and X6, which differed only in the 1,5 per

cent copper contained in X6, and which contained about 0,3 per cent nitrogen, had a very similar corrosion resistance, indicating that copper additions had little effect in this particular chloride environment. The difference in the resistance to pitting attack is also apparent in Figure 16, which shows the appearance of the specimens after 4 hours at 52°C.

Metallographic examination of the pitted specimens showed that the austenite phase was generally attacked during the pitting test (Figure 17) although, once a pit had started it consumed both ferrite and austenite (Figure 18). Alloy X7 was found to have become pitted extensively at 52°C, and not only suffered serious edge pitting but was also covered with several bands of coalesced pits. In some of the X7 specimens, these bands appeared to have developed and grown in the direction of gravitational force.

## DISCUSSION

### Manganese and Copper in Duplex Stainless Steels

Kirchner and Uhrenius<sup>14</sup>, and Rivlin and Raynor<sup>15</sup> have reviewed the Fe-Cr-Mn system; other discussions are available in Hochmann<sup>16</sup> and elsewhere<sup>17</sup>. Manganese is generally considered to be an austenite-forming element; it is most effective in concentrations of up to 4 or 5 per cent, and is less effective in greater amounts. Some authorities

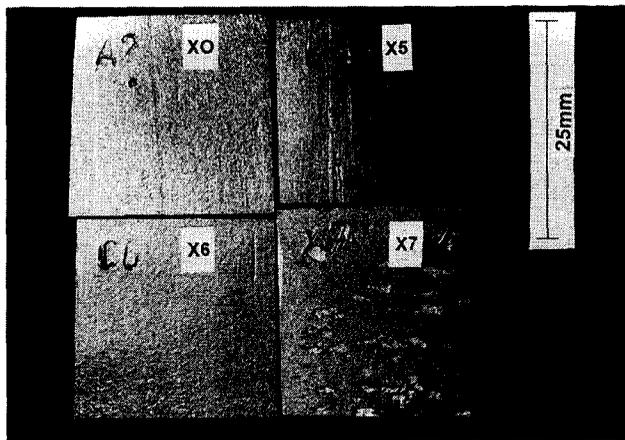


Figure 16—Appearance of coupons of wrought 22 per cent chromium alloys after an exposure of 4 hours to FeCl<sub>3</sub> solution at 52°C

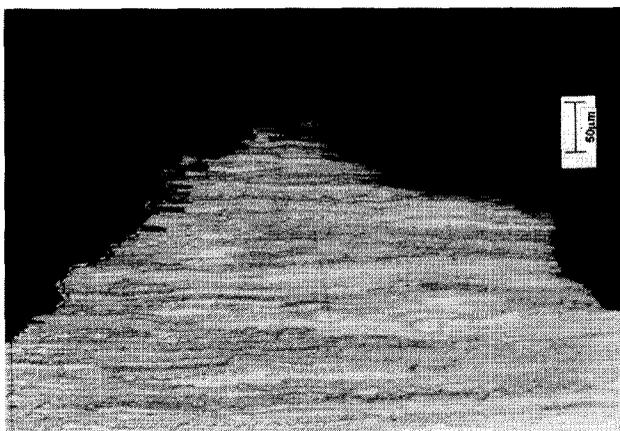


Figure 17—Selective attack of the austenite phase in alloy X0 after immersion in FeCl<sub>3</sub> at 52°C

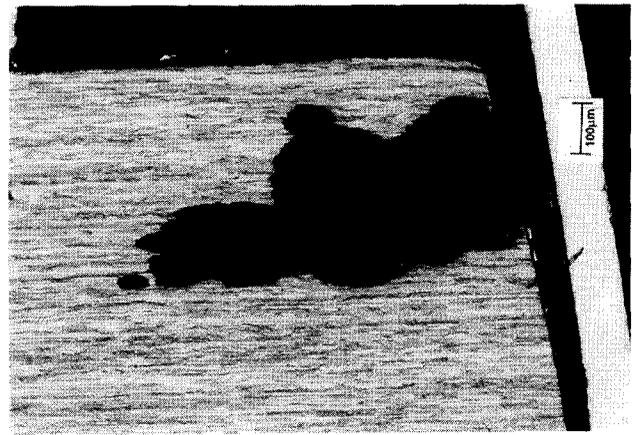


Figure 18—Cross-section through a typical corrosion pit developed in alloy X0 after an exposure of 4 hours to FeCl<sub>3</sub> solution at 52°C

have stated that only the first 2 per cent manganese functions effectively as an austenite former<sup>18</sup>, or that, in certain alloys, manganese is actually a weak ferrite former<sup>16</sup>. The weak austenite-forming tendencies of manganese can be clearly seen in Figures 19 and 20, which show the 950°C and 1200°C isothermal sections through an assessed Cr-Mn-Fe phase diagram<sup>15</sup>. Clearly, manganese additions scarcely enlarge the  $\gamma$  phase field beyond about 15 or so per cent chromium, even at contents as high as 30 per cent manganese<sup>16</sup>. However, they do reduce the area of the  $\alpha$  phase field, especially at temperatures between about 1000 and 1200°C. For example, a variation in the manganese content from 0 to 20 per cent moves the position of the  $\alpha/\gamma + \alpha$  phase boundary at 1000°C from 12 to about 25 per cent chromium<sup>15</sup>. This has the net effect of producing duplex microstructures in alloys that would otherwise be ferritic. Manganese is therefore an effective shrinker of the  $\alpha$  phase field, and should be useful in promoting duplex microstructures. Manganese additions to stainless steels also increase the solubility of nitrogen in the molten state, and Roscoe<sup>1</sup> considers that this, rather than its austenite-forming power, is the commonest reason for its addition to duplex stainless-steel compositions.

Copper is well known as an additive to stainless steels. A preliminary Fe-Mn-Cu ternary phase diagram is available in the review by Rivlin<sup>15</sup>. Although small additions of copper are known to improve the corrosion resistance of *ferritic* stainless steels in some media<sup>19</sup>, copper is rarely added to those alloys. However, a few austenitic and duplex stainless steels contain significant amounts of copper. Examples of austenitic or duplex stainless steels with significant copper additions include 904L (1,5 per cent copper), Carpenter 20Cb3 (3 per cent), CDM4CU (3 per cent), Uranus 52N (1,5 per cent), and Ferralium alloy 255 (1,7 per cent)<sup>1,20,21</sup>.

In general, copper additions are found to reduce the corrosion rate of alloys in solutions of reducing acids, especially sulphuric acid<sup>21</sup>. The mechanism appears to involve the precipitation of metallic copper on the surface of the alloy, and the consequent movement of the corrosion potential into the passive range<sup>5,19,21,22</sup>.

Copper additions have been claimed to be either slightly beneficial<sup>5</sup> or detrimental<sup>22</sup> with regard to stress-corrosion

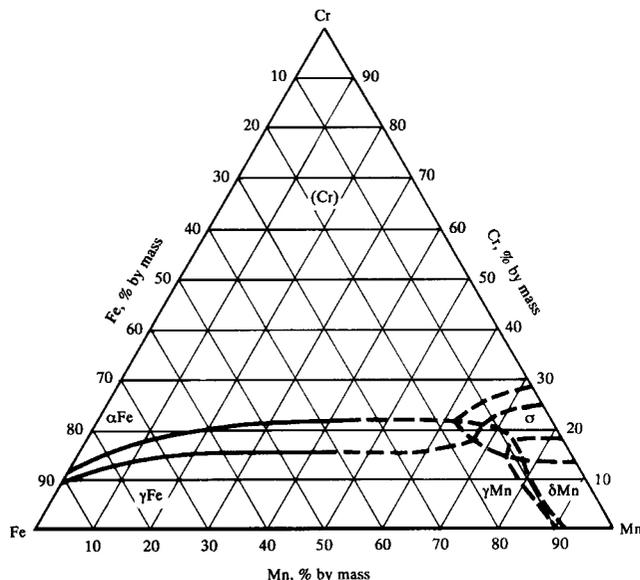


Figure 19—Isothermal section through the Fe-Cr-Mn ternary phase diagram at 950°C (after Rivlin<sup>15</sup>)

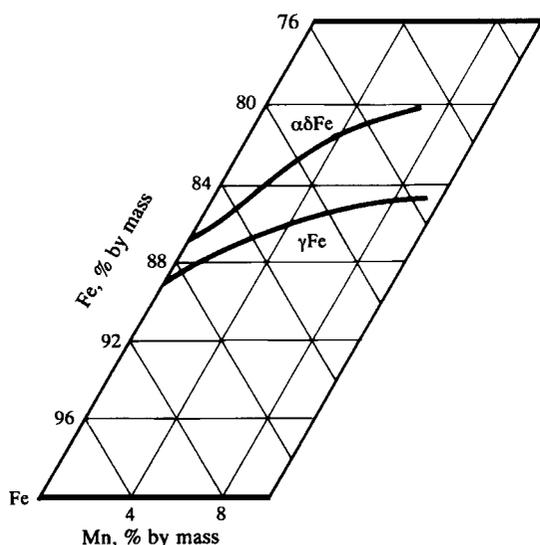


Figure 20—Isothermal section through the Fe-Cr-Mn ternary phase diagram at 1200°C (after Rivlin<sup>15</sup>)

cracking. They are said to be beneficial with regard to crevice corrosion in chloride solutions<sup>1,22</sup>, but the effect is not dramatic and may depend on the presence of molybdenum<sup>5</sup>. The addition of copper to austenitic and duplex stainless steels improves the pitting behaviour in sodium chloride solutions<sup>1,22</sup>. However, copper additions provided no improvement in the ferric chloride test when applied to the present experimental alloys.

### Existing Duplex Stainless Steels of High Manganese Content

An Armco patent describes a duplex stainless steel containing about 4,5 per cent manganese and 0,75 per cent copper<sup>18</sup>. This alloy was apparently developed for both wrought and cast applications, and is claimed to have the special advantages that it is resistant to the formation of  $\sigma$ -phase and 475°C embrittlement, and that it needs no heat treatment after casting. Exhaust manifolds are mentioned in

the patent as a possible application. It can be seen from Table IX that the alloy is of the lean type, and is similar to the present experimental alloy X1, except that it contains very little molybdenum and copper. The alloy claimed in the patent is also very similar to the pre-existing Soviet alloy<sup>23</sup> 06KH18G8N3M2T.

Guha<sup>24</sup> has patented a duplex stainless steel containing 24 per cent chromium, 5 per cent nickel, 6 per cent manganese, 2 per cent copper, and 0,18 per cent nitrogen. The particular advantage claimed for this alloy is that it does not have to be solution heat-treated after casting, rolling, or welding. Guha also claims that the manganese addition retards the precipitation of intermetallic phases. The range of compositions claimed in this patent is rather broad, but does not cover the experimental alloys described in this paper, generally because the latter have chromium contents of less than 23 per cent.

There are a number of Soviet duplex stainless steels that contain comparatively large amounts of manganese or copper. It is not known whether these alloys are still in production, how much is produced, or what their applications are. Examples are listed in Table IX, and are drawn from the *Handbook of Soviet Alloy Compositions*<sup>25</sup> and Babakov<sup>23</sup>. Alloys 1KH18N3G3D2L and 10KH18N3G3D2L are casting alloys, a feature indicated<sup>25</sup> by the presence of the suffix L. Since none of the alloys listed contains molybdenum, they could be expected to possess poorer pitting resistance than the generic Western 2205 alloy.

Table IX  
Patented or commercial duplex stainless steels of high manganese content

Alloy	C	Mn	Si	Cr	Ni	Mo	Cu	N	Ref.
Armco patent	0,04	4,6	1,0	19,3	2,5	0,3	0,8	0,10	18
Guha patent	0,05	6,0	1,0	24,0	5,0	2,5	1,8	0,18	24
0KH22G6AN5	0,03	6,6	0,4	22,5	4,9	0	0	0,24	25
0KH22G8AN5	0,03	8,3	0,4	22,6	5,1	0	0	0,025	25
1KH18N3G3D2L	0,1	2,8	0,5	18,5	3,3	0	2,0	0	25
1KH18N2AG5	0,1	5,0	0,8	18,5	2,0	0	0	0,20	25
10KH18N3G3D2L	0,11	2,8	0,5	18,8	3,3	0	2,2	0	25

### Prognosis for the Experimental Alloys

The corrosion resistance and mechanical properties of duplex stainless steels depend closely on the ratio of austenite to ferrite in the microstructure<sup>18,25,26</sup>. While the older commercial alloys like type 329 and CDM4CU usually contain 60 or 70 per cent ferrite<sup>2</sup>, the optimum ferrite content for most modern duplex stainless steels seems to be between 45 and 50 per cent by volume<sup>2,26</sup>. Only the X7 alloy (49 per cent ferrite) met this criterion in the present work, although the X4 and C4 alloys were tested in the 52 per cent ferrite condition. This implies that the optimum properties of the experimental alloys may not have been discovered, and the results given should possibly be regarded as conservative.

The lower nickel contents of the experimental alloys ensure that they would cost slightly less than the existing duplex and super-duplex stainless steels in the event of a nickel price excursion. In addition, the experimental alloys are significantly superior to the 2205 type of alloy in dilute sulphuric acid, and appear to have superior resistance to

chloride-induced pitting. It should be noted, however, that many aspects of these experimental alloys have not yet been evaluated, and that they are not yet ready for commercial exploitation. Factors such as formability, weldability, and resistance to stress-corrosion cracking have not been investigated. Nevertheless, it is believed that they may hold promise as reduced-nickel substitutes for the generic 2205 type of alloy. Product forms that could be envisaged include centrifugally-cast piping, and plate and sheet.

## CONCLUSIONS

1. Wrought duplex stainless steels in which part of the nickel content is replaced with manganese, nitrogen, and copper can be produced under experimental conditions, but the copper content must not exceed about 2 per cent.
2. The rate of corrosion of high-manganese duplex stainless steels in sulphuric acid solutions is noticeably reduced by additions of copper, and some of the experimental alloys possessed better corrosion resistance in these environments than the 2205-type alloy.
3. Resistance to pitting attack in ferric chloride was governed primarily by the chromium, molybdenum, and nitrogen contents, and copper had little effect in that environment.
4. Manganese is a weak austenite former, but its addition to Fe-Cr-Ni alloys contracts the ferrite phase field. Manganese is therefore an effective promoter of duplex microstructures.

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## REFERENCES

1. ROSCOE, C.V., and GRADWELL, K.J. The history and development of duplex stainless steels 'All that glisters is not gold'. *International Conference on Duplex Stainless Steels*. Netherlands, The Hague, 1986. pp.126-135.
2. SOLOMON, H.D., and DEVINE, T.M. Duplex stainless steels—a tale of two phases. *Duplex Stainless Steels Conference Proceedings*. Lula, R.A. (ed.). Metals Park (USA), American Society for Metals, 1983. pp. 693-756.
3. WARD, I.A. *The performance of a new high strength, low cost duplex stainless steel*. Institute of Metals and Materials, 1987. pp. 433-436.
4. RALPH, M.D., and REDMOND, J.D. Practical guide to using duplex stainless steels. *Mater. Perf.*, 1990. pp. 58-60.

5. SEDRICKS, A.J. *Corrosion of stainless steels*. New York, John Wiley & Sons, 1979.
6. FOURIE, J.W., and ROBINSON, F.P.A. Literature review on the influence of weld-heat inputs on the mechanical and corrosion properties of duplex stainless steels. *J. S. Afr. Inst. Min. Metall.*, vol. 90, no. 3. 1990. pp. 59-65.
7. CORTIE, M.B., and POTGIETER, J.H. The effect of temperature and nitrogen content on the partitioning of alloy elements in duplex stainless steels. *Metall. Trans. A*, vol. 22. 1991. pp. 2173-2179.
8. LIZLOVS, E.A. *Report RP-33-80-08*. Greenwich (USA), Climax Molybdenum Company, Jun. 1981.
9. POTGIETER, J.H., and CORTIE, M.B. Determination of the microstructure and alloy element distribution in experimental duplex stainless steels. *Mater. Charact.*, vol. 26. 1991. pp.155-165.
10. VANDER VOORT, G.F. The metallography of stainless steels. *J.Met.*, Mar. 1989. pp. 6-11.
11. ASTM std G31, Laboratory immersion corrosion testing of metals.
12. ASTM std G48, Pitting and crevice corrosion resistance of stainless steels and related alloys by use of ferric chloride solution.
13. ANON. Avesta 2205. *Information pamphlet* 9163. Sweden, Avesta AB, undated.
14. KIRCHNER, G., and UHRENIUS, B. Experimental study of the ferrite/austenite equilibrium in the Fe-Cr-Mn system and the optimization of thermodynamic parameters by means of a general mathematical method. *Acta Metall.*, vol. 22. 1974. pp. 523-533.
15. RIVLIN, V.G., and RAYNOR, G.V. Phase equilibria in iron ternary alloys. 9. Critical review of constitution of ternary systems Fe-Mn-X (X=Ti, V, Cr, Co, Ni, Cu). *Int. Met. Rev.*, vol. 28, no. 1. 1983. pp. 23-64.
16. HOCHMANN, J. The role of manganese additions in austenitic stainless steels. *Mater. Techn.*, Dec. 1977. pp. 69-87.
17. LULA, R.A. *Manganese stainless steels*. Paris, The Manganese Centre, 1986.
18. DANIELS, J.A., DOUTHETT, J.A., and TACK, J.G. Duplex stainless steels with high manganese. *S. Afr. Pat.*, no. 890088. 1989.
19. MURASE, S. The influence of copper additions on the corrosion resistance of stainless steels. Johannesburg, University of the Witwatersrand, M.Sc. thesis, 1991.
20. ANON. Duplex grades. A new stainless steel family. France, Creusot-Loire Industrie, 1989.
21. SRIDHAR, N. Behaviour of high-performance alloys in sulphuric acid. *Mater. Perform.*, Mar. 1988. pp. 40-46.
22. LIN, H., TSAI, W., LEE, J., and HUANG, C. The electrochemical and corrosion behaviour of austenitic stainless steel containing Cu. *Corr. Sci.*, vol. 33, no. 5. 1992. pp. 691-697.
23. BABAKOV, A.A., and GOLOVANENKO, S.A. Basic properties and production technology for nickel-free and low-nickel stainless steels. *Stahl*, vol. 6. 1977. pp. 539-546.
24. GUHA, P. High chromium duplex stainless steel, *US Pat.* no. 4, 657, 606.1987.
25. ANON. *Handbook of Soviet alloy compositions*. U.S. Air Force Systems Command, Foreign Technology Division, 1980.
26. ECKENROD, J.J., and PINNOW, K.E. Effects of chemical composition and thermal history on the properties of alloy 2205 duplex stainless steel. *1984 ASM International Conference on New Developments in Stainless Steel Technology*. Metals Park (USA), American Society for Metals, 1984. Paper 8410-029.