Note

Low Manganese Corrosion Resistant Steels

Corrosion resistance of Cr–Ni stainless steels is often limited by their susceptibility to pitting-attack in chloride containing media. It has been confirmed by many research centers^{1–17)} that inclusions of manganese sulfide or duplex oxides–manganese sulphides act as pitting initiation sites.

The idea of improving resistance to pitting of stainless steels by eliminating the most harmful inclusions has found laboratory^{9,13,15)} and even some practical¹⁴⁾ confirmation. The elimination of MnS_x inclusions from steels can be achieved on various ways, namely by;

- adding an element that forms chemically more stable and thus less detrimental sulfides, which are immune to chloride solutions.
- decreasing S content or Mn content in steel, alternatively, to approach the level below the solubility product of MnS .

The last possibility has been explored by Degerbeck¹⁴⁾ to produce special steel grades with low Mn content ($\sim 0.3\%$ Mn) and 2.7% Mo, which exhibited higher resistance to pitting and crevice corrosion, than AISI 316 and AISI 304. He found that lowering Mn content in steels down to $\sim 0.2\%$ doubles the beneficial effect of increasing Cr content.¹⁴⁾ We have attempted to explore this observation to develop alloys with low Mn content, by a factor of 10 or more as compared to Mn in the commercial steels, and with low or none Mo addition. We have tried to compensate absence of Mo by some increase in Cr content and by an additional alloying with Ti or Si to retain a good resistance of the modified steels against pitting corrosion (Table 1). Chemical composition of two commercial steels, used for a com-

parison, is given in Table 2. The steels were hot worked into rods, $\phi=12$ mm, and then solution annealed at 1050°C and water quenched.

Fig. 1 summarizes the results of electrochemical measurements of the pit nucleation potential, E_{np} , for all the materials investigated in 0.5 M NaCl , at 25°C . The E_{np} values have been determined from quasistationary anodic polarization curves.¹⁸⁾ The diagram shows that the low Mn steel G-2 exhibits E_{np} value comparable with that for the commercial steel (II). The other low Mn steels exhibit nobler E_{np} values than those characteristic of the commercial steels thus inferring that the low Mn steels are more resistant to pitting than the commercial ones.

Careful examinations with the aid of an optical microscope and an X-ray microprobe analyzer JEOL JXA 3A of the samples' surface before and after the electrochemical experiments have revealed the following:

—In both groups of steels the most susceptible spots for pit nucleation are $(\text{Cr,Mn})\text{S}_x$ inclusions, or TiS_x inclusions in Ti bearing steels. However, the low Mn steels were found to be more resistant to pitting corrosion.

Composition of the inclusions, of the adjacent matrix and that of their boundary region is different for the two groups of steels, compare Figs. 2 and 3.

Fig. 1. Diagram comparing E_{np} values for the commercial and modified steels in 0.5 M NaCl .

Table 1. Chemical composition of modified low Mn steels.

Heat	Chemical composition (wt%)						Additional alloying elements
	C	Mn	P	S	Cr	Ni	
E-1	0.03	0.23	0.006	0.015	18.3	13.9	Ti-0.64
G-2	0.04	0.21	0.008	0.014	18.3	13.5	{Si-2.5; Mo-1.1
R-4	0.03	0.20	0.008	0.010	18.4	13.9	—
Z-7	0.04	0.31	0.006	0.014	18.7	14.6	{Ti-0.65; Mo-1.1

Table 2. Chemical composition of commercial steels. (wt%)

Steel	C	Mn	Si	P	S	Cr	Ni	Mo	Ti
(I) OH17N13M2T	0.040	1.40	0.60	0.028	0.015	16.8	12.3	2.6	0.22
(II) OOH17N14M2	0.020	1.96	0.33	0.022	0.012	17.6	14.7	2.8	—

Fig. 2. Line scan across a typical (Cr, Mn) S_x inclusion in the modified steel R-4, showing distribution of Mn, Mo, Cr and S within the inclusion and outside. X-ray microprobe analysis.
cpm: Counts per minute

Fig. 3. X-ray microprobe analytical results for a typical (Mn, Cr) S_x inclusion in commercial steel (II). Line scan across a typical inclusion showing distribution of Mn, Mo, Cr and S within the inclusion and outside.

Spatial distribution of various elements there affects composition of the passive film formed at these regions and, what follows, its stability in Cl^- containing solutions, as well as ability to repassivate. *E.g.* commercial steel (II) exhibits a high Mn level in the matrix adjacent to the (Mn, Cr) S_x inclusions and an abrupt drop of Cr concentration at the boundary matrix/inclusion (Fig. 3). This makes that region prone to pitting. The modified steel R-4 does not exhibit those features (Fig. 2), what results in its higher resistance to pitting than steel (II), (Fig. 1).

Local effects on inclusions in the modified steels are so important for their pitting resistance that they obscure a possible influence of $Mo < 1.2\%$. So, E_{np} for Z-7 and R-4 are comparable, Fig. 1, in spite of the difference in Mo content in the both steels.

Effect of Ti is very beneficial. As these steels contain low C, the Ti modifies composition of the *sulfide inclusions*, and remains in the *matrix*, thus affecting their ability to passivate. Therefore, at low Mn level the region matrix/inclusion exhibits improved stability: E_{np} for E-1 is higher than for steel (I), Fig. 1.

Surprisingly G-2 containing Si+Mo exhibits lower E_{np} than the other modified steels (Fig. 1). Some metallurgical factors may be responsible for this; the problem requires further investigation.

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