Influence of Manganese on the Properties of a Vanadium-bearing Ferritic Stainless Steel

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For the purpose of further increasing toughness, the influence of manganese contents up to 4% was investigated in a 4% vanadium-bearing experimental ferritic stainless steel. The tensile and formability properties were also studied. The corrosion properties were measured using electrochemical techniques in 1 N H₂SO₄ and 3.5% NaCl solutions.

No marked effect was found on the tensile and formability properties. In contrast, manganese has a strong detrimental effect on the general and localized corrosion properties of this 4% vanadium alloy. The passivation characteristics in normal sulphuric acid are much poorer. However, spontaneous passivation occurs in this environment where the manganese content is 0.1%. Similarly, the propensity to pitting corrosion is greatly improved at low manganese levels, with pitting potentials superior to both type 304 and 316L stainless steels.

KEY WORDS: stainless steels; ferritic; vanadium; manganese; mechanical properties; corrosion properties.

1. Introduction

In the past, manganese has been used in carbon–manganese steels¹⁾ to achieve grain refining of the ferrite and reduce the grain-boundary carbide thickness, *i.e.*, to improve toughness. In low silicon-steels (0.01 to 0.07% Si), manganese has also been reported to have a significant effect on the impact properties, with a 40°C drop in the impact transition temperature.²⁾

In ferritic stainless steels, however, the use of manganese as an alloying addition has been kept to a minimum. In fact, manganese, (like vanadium), is not commonly added to ferritic stainless steels. Manganese is not regarded as a useful alloy addition as such, and American Iron and Steel Institute (AISI) grades specify a maximum limit of 1% manganese. In the 300 series of stainless steels, manganese additions are allowed up to 2% maximum, as a useful and more economical austenitizer than nickel. In 1979, Japanese workers³⁾ developed an 18% Cr ferritic stainless steel with manganese additions of up to 2%, having improved toughness of sheets and plates in the welded condition. Little effect, however, was observed on the formability of the cold-rolled and annealed sheet product.

Recent work⁴⁾ has shown the potential of vanadium in improving the impact roughness and localized corrosion performance of an 18% Cr ferritic stainless steel. The combined effects of vanadium and manganese on the properties of this material are worthy of investigation.

In this paper, the effects of manganese additions (up

to 4%) are investigated on the toughness and formability properties of a vanadium-bearing (4% V) 18% Cr ferritic stainless steel in sheet and plate form. Reference to the modified Schaeffler diagram⁵⁾ shows that up to 4% manganese can be accommodated in 18% Cr ferritic stainless steels without forming austenite. The general and pitting corrosion properties were also examined. In addition, the opportunity was taken to assess the influence of nickel on the 4% V alloy. It is well known in the literature that nickel improves resistance to cleavage fracture in ferrite by increasing the surface energy term (τ) in the Cottrell–Petch equation:

$$(\sigma_0 d^{1/2} + k_y)k_y = \beta \mu \tau,$$

where β is a constant related to stress state, τ is the effective surface energy of the crack, μ is the shear modulus, d is the grain diameter, σ_0 and k_y the friction stress and Petch slope respectively.⁶⁾

2. Experimental Procedure

Experimental ingots of about 10 kg, and with the chemical composition given in **Table 1**, were cast in a vacuum induction furnace. The (C+N) levels, which markedly influence the toughness of the alloy, were maintained as much as possible within the 200–300 ppm range, which is typical of electric-arc and argon–oxygen decarburization (AOD) practice. The carbon levels, which determine the extent of intergranular corrosion, are within a 50 ppm experimental error.

The ingots were surface-dressed and homogenized at

Table 1. Experimental alloy compositions.

Alloy No.	Nominal Comp.	C (ppm)	Si (%)	Mn (%)	Cr (%)	Mo (%)	V (%)	N (ppm)
49	4V-OMn	250	0.21	0.09	18.6	0.03	4.20	30
50	4V-1Mn	200	0.31	0.97	18.6	0.03	4.14	30
51	4V-2Mn	160	0.30	2.00	18.6	0.03	4.12	40
52	4V-3Mn	150	0.32	2.89	18.7	0.02	4.10	30
53	4V-4Mn	140	0.30	3.89	18.6	0.02	4.10	40
80	4V-2Ni	200	0.20	0.05	18.5	0.04	3.98	30

Balance Fe; residuals (Cu, Ni, *etc.*) 0.1 max. total; S+P 0.02 max.

1 100°C for 2 h, then hot-rolled to 12 and 6 mm thick plates, with a 30 % reduction per pass. For all alloys, the finish hot-rolling temperature was around 900–950°C; the plates were then air-cooled. For sheet processing, hot-rolling to a 4 mm-thick plate material was carried out, with a finish hot-rolling temperature of 900–950°C, followed by spray quenching to a simulated coiling temperature of 700°C, and then slow cooling in a vermiculite bed. Intermediate annealing of the 4 mm plates was done at 815°C for 30 min, and followed by water quenching. The annealed and pickled plates were cold rolled to 1 mm thickness (about 75 % reduction). Sub-size (5 × 10 × 55 mm) T-L [ASTM E399-83] Charpy specimens and (100 × 20 × 10 mm) fracture-toughness bend test specimens were cut from the 6 and 12 mm thick plate material respectively, annealed at 850°C for 30 min, water quenched, and then notched in the case of Charpy specimens. Although this heat treatment may not be optimum, it is based on sub-critical annealing of type 340 stainless steel.^{3,4,7)}

Standard tensile test specimens (50 mm gauge length), Erichsen, and Swift test specimens were also cut from the 1 mm thick sheet material, and final-annealed at 850°C for 30 min and water quenched.

Metallographic examination of the samples was carried out on annealed material cut from the Charpy and tensile specimens. The polished longitudinal sections were electrolytically polished in concentrated HNO₃ to reveal carbides and grain boundaries.

Potentiodynamic scans were performed on each alloy using a potentiostat system and a PARC-273 corrosion-measurement system. A conventional three-electrode system was used. The test specimens were ground to a 1200 grit finish using silicon carbide papers, and washed with acetone prior to the testing. Test solutions of 1 N H₂SO₄ and 3.5% NaCl were prepared from reagent-grade chemicals and distilled water. The solutions were purged with high-purity nitrogen gas for at least one hour before each test was started, and continuously throughout the measurement period.

In order to avoid the formation of crevices, which would interfere with the pitting-potential measurements, a modified electrode holder, based on the Avesta pitting cell,⁸⁾ was used for all cyclic polarization scans. A fast scan rate of 7.2 V/h was used for the tests in sulphuric acid and the pitting tests in chloride media (Some of the more promising alloys were retested at the slow rate which conforms to ASTM G61 *i.e.* 0.72 V/h.). All the potential values quoted in this work are with respect to

Fig. 1. Microstructure of the 3 % Mn vanadium-bearing plate alloy (No. 52). Note the formation of sub-grains and fine dispersion of intragranular carbides. ASTM 1 to 2.

the saturated calomel electrode.

3. Results and Discussion

3.1. Microstructure

The plate alloys containing 3 and 4 % manganese (Nos. 52 and 53 respectively) showed a fully ferritic microstructure with elongated grains indicating a recovery process only and not recrystallization. Similar features to those found in previous work⁴ were present, *i.e.* sub-grain formation, fine dispersion of intragranular carbides, and an ASTM grain size of 1 to 2 (**Figs. 1 and 2**). In contrast, recrystallization was more evident in the 1 and 2 % manganese alloys (Nos. 50 and 51 respectively) with more equiaxed and uniform grains and an ASTM grain size of about 4 (**Figs. 3 and 4**). All the sheet alloys exhibited a recrystallized microstructure, with a mixed grain size in some cases. An example for the 4 % manganese alloy (No. 53) is shown in **Fig. 5**.

3.2. Mechanical Properties

Since the focus of attention was on the impact and fracture toughness of the plate material, only these are discussed here. The effect of manganese additions on the impact toughness of the alloys were assessed from the transition curves shown in **Fig. 6**. A graph of the Ductile-to-Brittle Transition Temperature (DBTT) as a function of manganese content is shown in **Fig. 7** (35 Joule criterion). Due to experimental scatter, a temperature interval is quoted for the DBTT. It can be seen that, with the exception of the 3 % Mn alloy (No. 52), the DBTT increases with manganese content. The DBTT for alloy No. 52 (**Fig. 6**) show an exceptionally

Fig. 2. Microstructure of the 4% Mn vanadium-bearing plate alloy (No. 53). As in Fig. 1.

Fig. 4. Microstructure of 2% Mn vanadium-bearing plate alloy (No. 51). As in Fig. 3.

Fig. 3. Microstructure of the 1% Mn vanadium-bearing plate alloy (No. 50). Recrystallization is marked by more equiaxed and uniform grains. ASTM about 4.

Fig. 5. Recrystallized microstructure obtained from the 4% Mn vanadium-bearing sheet alloy.

large scatter. Nickel has a negligible influence on the DBTT for the 4% V alloy (No. 80). Nickel reduces the amount of grain boundary precipitation by trapping interstitial atoms in the lattice,⁹⁾ whereas vanadium removes chromium carbides at the grain boundaries and

precipitates vanadium carbides within the grain.¹⁰⁾ It is possible that if nickel reduces the amount of grain-boundary precipitates, then no improvement is gained by adding nickel to vanadium-bearing alloys.⁹⁾

The influence of grain size on the DBTT is well known, and this may have some effect on the results. However,

Fig. 6. Impact energy transition curves for 4% V alloy as a function of Mn content. (a) 0% (No. 49), (b) 1% (No. 50), (c) 2% (No. 51), (d) 3% (No. 52), (e) 4% (No. 53).

the effect of stabilizer precipitates (vanadium carbonitrides), in particular their size and distribution, may be more important.¹¹⁾ Cracked precipitates are suitable initiation sites for brittle fracture. In the presence of

vanadium, the observed detrimental effects of manganese may be due to the hardening of the ferrite matrix (Table 2).

The plane-strain fracture-toughness tests (K_{Ic}) show-

Fig. 7. DBTT (35J) variation with Mn content for 4% vanadium alloy.

Table 2. Sheet formability data (results averaged over three measurements).

Alloy No.	Proof stress 0.2% (MPa)	Vickers HV30	$r^{(1)}$	$n^{(2)}$	UTS (MPa)	Elong (%)	Erichsen (mm)	LDR ⁽³⁾
49	287	165.7	0.86	0.22	460	26	9.2	2.0
50	308	152.9	0.79	0.23	473	28	9.9	2.0
51	309	154.1	0.87	0.22	481	27	9.8	2.2
52	321	164.5	0.67	0.22	480	27	10.3	2.0
53	323	173.5	0.84	0.23	475	24	10.1	2.0

¹⁾ Plastic anisotropy factor measured only in longitudinal direction at 15% strain.

²⁾ Work hardening index calculated for the strain range 0.05 to 0.15.

³⁾ Limiting draw ratio.

ed no trend with increasing manganese, and were in the range 30–50 MPa $\sqrt{m}$ which is similar to those from previous work on vanadium additions to 18% Cr ferritic stainless steels.⁴⁾ The main benefit of vanadium as an alloying addition is increased resistance to crack initiation. Fracture is initiation-controlled in these relatively low-strength steels, and the size and distribution of vanadium carbonitride particles decreases the tendency to brittle fracture. Further alloying with manganese or nickel in the presence of vanadium improves neither the impact toughness nor (in the case of manganese) the fracture toughness.

The mechanical and formability data for the alloy in sheet form are shown in Table 2. The proof stress increases slightly with increasing manganese, probably due to solid-solution hardening. The elongation values fit into a scatter band of 25 to 30% which is fairly typical of 18% Cr steels. The work-hardening indices average around 0.23, which is fairly typical of steels with a ferrite matrix. A slight increase in the Erichsen value is noticeable with increasing manganese, but in general the addition of manganese causes little change.

3.3. Corrosion Properties

Although ferritic stainless steels are not designed for application in H₂SO₄, anodic polarization tests were carried out in this medium to serve as a measure of the general corrosion performance of the material in other

Table 3. Anodic polarization data in de-aerated 1 N H₂SO₄ at 25°C.

Alloy No.	Scan rate (mV/min)	E_{corr} (mV)	i_{corr} (μ A/cm ²)	i_{crit} (μ A/cm ²)	E_{pass} (mV)	i_{pass} (min.) (μ A/cm ²)
49	12	+10	—	—	—	6.8
50	120	−544	795	71 210	−399	30.6
51	120	−546	980	80 940	−382	32.7
52	120	−546	1350	88 280	−404	73.4
53	120	−582	185	40 380	−436	118.5
316L	12	−301	4	11	−265	2.7

Fig. 8. Anodic polarization curves for 18Cr-4V stainless steels in 1 N H₂SO₄ at 25°C, showing the effect of manganese.

environments. The results are given in Table 3.

Previous work¹²⁾ showed that the i_{crit} values decrease somewhat with increasing vanadium content. These results indicate an increase in both the passivating tendencies and the active-state corrosion resistance of the stainless steel alloys.¹³⁾ The addition of manganese however, does not show an effect on the i_{crit} values at the levels studied. The detrimental influences of manganese on $i_{pass}(min)$ can be clearly seen in Fig. 8. Passivation in H₂SO₄ will be difficult (if not impossible) in practice, due to the i_{crit} values measured for alloys 50–53. This is evident in high active corrosion rates (5–9 mm/y) where i_{corr} was measured from the Tafel slope using the slow scan method. The results obtained on a type 316L austenitic stainless steel are also shown in Table 3 for comparison.

The 4%V-0%Mn alloy (No. 49) does not show any anodic peak with its E_{corr} in the passive range. This result was again confirmed in further tests, and Fig. 9 shows this effect. Spontaneous passivation in 1 N H₂SO₄ has been reported¹⁴⁾ for a 18% Cr ferritic with the addition of 8% Mo. In this study, spontaneous passivation can be ascribed to the favourable combination of 4% vanadium and a low manganese content (0.1%). In this case, there may be a sharp decrease in i_{crit} values as the manganese level is lowered below 1%. This increase of i_{crit} values as the manganese level is lowered below 1%. This increase of i_{crit} with increasing manganese has been reported for austenitic stainless steels.^{13,15)} Further work is required to clarify the combined effects of vanadium,

Fig. 9. Anodic polarization curves for 18Cr-4V-0Mn (alloy No. 49) and type 316L stainless steel in 1 N H₂SO₄ at 25°C.

Fig. 10. Variation of the pitting potential with Mn content for 4% V alloys.

Table 4. Cyclic polarization data (3.5% NaCl at 25°C, fast scan rate).

Alloy No.	E_{pit} (mV)	E_{prot} (mV)	E_{corr} (mV)
49	776	429	-148
50	431	314	-137
51	404	350	-143
52	410	355	-148
53	381	262	-123
316L	324	-74	-190
0.4Mn*	558	144	-203

* Composition: Cr, 18.4; V, 4.05; Mn, 0.42; C, 250 ppm; N, 40 ppm.

manganese, and molybdenum in an 18% Cr ferritic stainless steel. In practice, passivation for this alloy is possible even in relatively stagnant solutions. Figure 9 also shows that the type 316L stainless steel has a lower passive current density. This is ascribed to its much higher content of alloying elements.

The results of the pitting scans in 3.5% sodium chloride are shown in Table 4 and Fig. 10. A 400 g melt at a manganese level of 0.4% was manufactured to obtain an extra data point. Although the fast scan rates chosen will have an influence on the measured pitting potentials, it is assumed that there is no change in the ranking of the alloys. Again the beneficial effect of low manganese (0.1% Mn for alloy No. 49) can be seen. The 4%V-

0%Mn alloy (No. 49) displays pitting potentials superior to type 316L stainless steel (slow scan values of 683 mV for alloy No. 49 as against 487 mV for 316L). It is known that vanadium sulphides are far more insoluble in acids than manganese sulphides,¹⁶⁾ and this may render pit initiation more difficult. It is possible that the manganese content of the alloy could be low enough for vanadium to substitute almost completely in the sulphide inclusion composition, thereby increasing the pitting potential. Ideally, the manganese content should be limited for optimum corrosion properties in these vanadium-bearing ferritic stainless steels.

Types 304 and 316 austenite stainless steels may suffer premature failure due to pitting, stress-corrosion cracking (SCC), or corrosion fatigue (CF). These failure modes can occur in relatively mild or moderate environments where chlorides (or other halide ions) are present. A cheaper vanadium-bearing stainless steel may prove more cost-effective in such environments. Also, due to its relatively high pitting potential, the vanadium steel may prove a better choice than type 316 in architectural applications, e.g. stainless steel panelling. Success in these applications may lead to increased acceptance of vanadium-bearing stainless steels in the marketplace.

4. Conclusions

The main conclusions obtained from this work are as follows.

- (1) In 4% vanadium alloys, the DBTT follows an increasing trend with manganese content.
- (2) The addition of 2% nickel to a manganese-free 4% V alloy caused little change to the DBTT.
- (3) Manganese has no marked effect on the tensile and formability parameters.
- (4) In contrast, manganese has a strong detrimental effect on the general and localized corrosion properties.
- (5) A low-manganese (<0.1%) 4% V ferritic stainless steel has superior corrosion performance to the commercial 18% Cr austenitic stainless steels.
- (6) Major improvements to the pitting potential are obtained if the manganese level is kept below 0.2 to 0.3%.

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