THE EFFECT OF VANADIUM AND OTHER
ELEMENTS ON THE MECHANICAL
PROPERTIES AND CORROSION
RESISTANCE OF FERRITIC
STAINLESS STEELS

by

R.D. DAVIES

A thesis submitted to the Faculty of Engineering,
University of the Witwatersrand, Johannesburg,
in fulfilment of the requirements for the degree
of Master of Science in Engineering.

March, 1983

DECLARATION

The work reported in this thesis was carried out by the author between 1980 and 1983. Except for the preparation of the alloys and the determination of their tensile properties, which was done at the University of Sheffield on instructions from the author, most of the work involving the selection of the alloys, the determination of their impact and corrosion resistance properties, and the interpretation of the results was performed by the author.

Included in this thesis are three supporting publications covering various aspects of the research reported herein.

The thesis has not been submitted before for any degree or examination in any other University.

Ronald   Douglas   Deurel

_____31st_____ day of ____March____, 19 83 .

ABSTRACT

The effect of vanadium, in the concentration range 1 to 4%, alone and
in combination with the other specific alloying elements titanium,
niobium, nickel, copper, molybdenum and silicon (maximum concentration
of 2% each) was examined in low-interstitial, 18% chromium ferritic
stainless steels (C + N = 84 to 168 ppm). Testing of the alloys
involved determination of their tensile and toughness properties,
passivity, and pitting, general and intergranular corrosion resistance.
Vanadium increased the tensile strength (except at the 2.6% level) and
markedly improved the toughness of the base 18% chromium alloy.
Stabilization with 0.1% titanium reversed the trend found for the
impact transition temperature in the 18Cr-V alloys. The addition of
nickel and copper to the Cr-V-Ti alloys reduced the transition
temperature, while molybdenum and silicon raised the temperature
slightly. Vanadium was found to have a variable effect on the
passivity in 1N H_2SO_4, producing the detrimental effect of lowering
the breakdown potential. Most of the other alloying elements,
particularly molybdenum, improved the passivity of the base Cr-V(-Ni)
alloy. Vanadium raised the pitting potential in 0.1N NaCl, but had a
detrimental effect in increasing weight loss in the $FeCl_3$ test.
Molybdenum was the most beneficial element as regards pitting resistance.
The most favourable alloy combination in resisting general corrosion
in HNO_3, H_2SO_4 and oxalic acid was 18Cr-4V-Ti-1.5Ni-1Cu. None of the
alloying elements was found to induce susceptibility to intergranular
corrosion in the Strauss test. The effect of the various alloying
elements on the mechanical properties are interpreted in terms of
participation and solid solution strengthening phenomena. Their effect
on the corrosion resistance is determined by the degree to which they
participate in passive film formation.

C O N T E N T S

(v)

1. INTRODUCTION

Most industrialized countries have been faced with the problem of
materials substitution at one time or another, and the subject is
regularly discussed in the literature because of the political
implications. There are many reasons for examining materials substi-
tution with the emphasis depending on the problems and local resources
of the particular country.

Molybdenum is well known for the beneficial effect it has on the
corrosion resistance of stainless steels, in particular the resistance
to pitting corrosion and to sulphuric acid. There are several factors
which favour the development of a local substitute for molybdenum,
these being the fact that South Africa must import all her requirements
of the metal, the essential role of the metal as an alloying element
in corrosion-resisting steels and high-strength low-alloy steels, the
highly fluctuating price of the metal, and lastly but perhaps most
importantly, the abundance in South Africa of the metal vanadium which
is one of the most promising substitutes for molybdenum.

The literature contains several references to the fact that vanadium
improves the pitting resistance of stainless steels (Tomashov et al.,
1964; Biefer, 1970; Lizlovs, 1974; also unpublished work by The Climax
Molybdenum Co., USA). Another useful property of vanadium when
compared to molybdenum is the improvement in impact properties conferred
on ferritic stainless steels (Aslund, 1977; Climax Molybdenum,
unpublished work).

Some of the earliest work on the effect of vanadium in stainless steels
was carried out in Germany in about 1929. In the original Krupp patent
(1929) covering the use of titanium as a preventative for intergranular
corrosion, vanadium was also assessed and was claimed to have a similar
effect. Later research by Riedrich and Huch (1930), however, showed
that vanadium was not very effective in inhibiting intergranular
corrosion. (Recent work by Climax th   (unpublished) indicates
that a minimum concentration of ʆ   in order to prevent
intergranular corrosion).

More recent research, since 1964, has examined other aspects of vanadium in stainless steels, in particular pitting corrosion and, to a lesser extent, impact properties. Tomashov et al. (1964), in a detailed study, showed that the pitting resistance of an 18Cr-14Ni stainless steel in 0.5N FeCl$_3$ increased significantly at vanadium levels above 2%, to the extent that corrosion was negligible at the 5% level (as was the case for molybdenum). In anodic polarization experiments, vanadium was found to increase the pitting potential in NaCl and HCl solutions. Vanadium also had a beneficial effect on the anodic polarization behaviour in H$_2$SO$_4$.

Biefer (1970) examined the effect of vanadium in a ferritic, Type 430, stainless steel. Although the maximum concentration studied was only 2.2%, the positive effects of vanadium in reducing corrosion in HCl and H$_2$SO$_4$, and in increasing the pitting potential at the 2.2% level, were noted. In FeCl$_3$ the corrosion rate was reduced slightly, but in HNO$_3$ the rate increased by approximately 100%.

Other workers have noted the beneficial effect of vanadium. Aslund (1977) found a synergistic effect between vanadium and titanium in increasing the pitting potential; he also noted that vanadium lowered the ductile-to-brittle transition temperature significantly. Unpublished work by Climax Molybdenum has shown that vanadium improves the corrosion resistance of 18 and 24% chromium stainless steels, although not to the same extent on a weight-for-weight basis as molybdenum. Climax Molybdenum has reported the beneficial effect of vanadium in reducing the impact transition temperature, especially after welding.

The primary objective of the present investigation was to examine the effect of vanadium on the mechanical properties and corrosion resistance of ferritic stainless steel. At the present time the most widely used molybdenum-bearing ferritic stainless steel is the so-called super-ferritic, Type 444, an 18Cr-2Mo titanium-stabilized alloy. A low-interstitial, 18% chromium base-alloy was used in this study so that the effects of vanadium could be compared by reference to the detailed results reported in the literature for the molybdenum-bearing Type 444.

In addition to the study of a straight Fe-Cr-V alloy, the effect of combinations with other elements such as nickel, silicon, copper and molybdenum, as well as stabilization with titanium and niobium, was also examined in an attempt to improve on the more deficient properties of ferritic stainless steels, namely, susceptibility to weld decay, poor resistance to reducing acids, and high ductile-to-brittle transition temperature. A total of sixteen vanadium-bearing alloys were prepared and experimental testing involved determination of their tensile, impact, pitting and general corrosion resistance properties.

In addition to the study of a straight Fe-Cr-V alloy, the effect of
combinations with other elements such as nickel, silicon, copper and
molybdenum, as well as stabilization with titanium and niobium, was
also examined in an attempt to improve on the more deficient properties
of ferritic stainless steels, namely, susceptibility to weld decay,
poor resistance to reducing acids, and high ductile-to-brittle
transition temperature. A total of sixteen vanadium-bearing alloys
were prepared and experimental testing involved determination of their
tensile, impact, pitting and general corrosion resistance properties.

2. SOME METALLURGICAL VARIABLES IN THE DESIGN
OF FERRITIC STAINLESS STEELS

Ferritic stainless steels have attracted continued interest from research workers for two main reasons : their resistance to stress-corrosion cracking and their low alloy content which makes their use in specific situations more economical when compared to austenitic stainless steels. However, the more widespread use of conventional ferritic stainless steels with carbon and nitrogen levels of 600-800 ppm, such as Type 430, is limited by their poor resistance to pitting corrosion and to corrosion by reducing acids, serious susceptibility to weld decay, and poor impact properties. One method of improving on these properties is to lower the carbon and nitrogen level which has the effect of reducing the amount of harmful precipitating phases. This approach is the basis for the development of the superferritic 18Cr-2Mo stainless steels which have a combined carbon and nitrogen content of about 300 ppm. Molybdenum has been added to these alloys despite to improve their resistance to pitting and crevice corrosion.

The present investigation involves essentially the replacement of molybdenum with vanadium in the superferritic 18Cr-2Mo, Type 444 alloy. However, in order to minimise the detrimental effects of intermetallic phases, a lower combined carbon and nitrogen level of 125 ppm was specified in the preparation of the experimental vanadium-bearing alloys. For comparative purposes the mechanical and corrosion resistant properties of the superferritic stainless steels are shown in Table 2.1. (The compositions of the alloys in the present study are given in Table 5.1.)

In this section various metallurgical factors affecting the mechanical properties of ferritic stainless steels will be discussed; a subsequent section will consider the effects of alloying on their corrosion resistant properties.

The mechanical properties of ferritic stainless steels are determined by their composition and the way in which they are processed (heat - treatment and hot - or cold - rolling). Since ferritic stainless

Table 2.1. Composition and Properties of Superferritic Stainless Steels

	Alloy Designation						
CrMoNi	18Cr-2Mo	26Cr-1Mo	26Cr-1Mo	26Cr-3Mo-4Ni	26Cr-2Mo-2.5Ni	28Cr-4Mo	29Cr-4Mo-2Ni
Common names	18-2, 444, Type 444	E Brite 26-1*, XM-27	26-1S, 26-1, XM-33	Remanit 4575*	SeaCure*, SC-1	29-4	29-4-2
UNS No.	S44400	S44625	S44626	—	—	S44700	S44800
ASME Code	Case 1825	Table UHA-23 Section VIII, Div 1	Case 1876	—	—	—	—
Carbon, wt.% max	0.025	0.01	0.06	0.025	0.025	0.010	0.010
Nitrogen, wt.% max	0.015	0.015	0.040	0.035	0.035	0.020	0.020
Typical C+N wt.%	0.04	0.312	0.04	0.040	0.040	0.018	0.018
Stabilizers	$(Ti+Cb)=0.20+4(C+N)$ min $=0.80$ max	0.15*	$Ti=0.20-1.00$, $+(C+N)$ min	$Cb=12(C+N)$ min $=0.60$ max	$(Ti+Cb)=0.20+4(C+N)$ min $=0.80$ max	none	none
Refining method	Argon-oxygen decarburization (AOD) Vacuum-oxygen decarburization (VOD)	Vacuum-induction melting (VIM)	AOD or VOD	VOD or AOD	AOD	VIM	VIM
Mechanical properties							
Yield strength MPa (10³ psi)	320(14)	345(50)	345(50)	483(70)	483(70)	515(75)	565(85)
Tensile strength MPa (10³ psi)	470(68)	455(70)	485(70)	620(94)	550(80)	620(90)	715(89)
Elongation %	36	32	30	79	30	22	22
Hardness Rb	80	84	85	83/94	40	97	97
Corrosion data							
	R*	R*	R*	F	F	R	R
	R	R	R	R	R	R	R
	R	R	R	R	R	R	R
Oxidation resistance							
	F	R				R	R
	F	F				R	R
	F	F				R	R
	F	F				F	F

1 The actual composition of data from various sources. Values given are not necessarily typical of commercial material and should not be relied upon as representative for the duration of metals ports.
2 E-Brite 26-1 is a trademark of Allegheny Ludlum Industries Inc.
3 Remanit 4575 is a trademark of Thyssen Edelstahlwerke AG.
4 SeaCure is a trademark of Crucible Materials Corp.
5 29-4 and 29-4-2 proposed to ASTM A 176-78, revision to 0.035 C max in ballot.
6 Cu requirements not in ASTM specifications but has been proposed by Allegheny Ludlum.

7 R, resistance; F, fair; P, poor, to type of corrosion shown.
8 Cu and Ni contents must be maintained at low levels to provide resistance to cracking in boiling oxidizing acids.
9 R indicates passive or self-repassivating with rates < 0.2 mm yr (0.006 in. yr); F indicates failure by higher corrosion rates.
10 Not recommended for strongly oxidizing solutions when Ti is used as a stabilizer.

Source: Ralph M. Davison and Robert F. Steigerwald, Climax Molybdenum Co., Div. Amax Inc. (March 1979)

5.

steels do not undergo phase transformation, cold work and annealing
are the only means of controlling their strength and grain size.
Several metallurgical reactions can embrittle ferritic stainless
steels with these being divided into those controlled by either
interstitial or substitutional elements.

Those reactions which involve interstitial elements usually occur
rapidly and influence short-term processes such as welding and
continuous annealing. Reactions involving the precipitation of
intermetallic phases, on the other hand, which occur at lower
temperatures and over long periods are more important during hot-
working, coiling and elevated – temperature exposure.

2.1. Carbon and Nitrogen

Many of the properties of ferritic stainless steels such as
ductility, toughness and intergranular corrosion are determined to
a large extent by the amount of carbon and nitrogen present. The
phase diagram of the iron-chromium system (Figure 2.1) shows that
ferrite which forms from the liquid in an 18% chromium steel does not
undergo a phase transformation on continued cooling. The gamma
region in the iron-chromium system is expanded by the addition of
elements such as carbon and nitrogen thus extending the range over
which austenite can form at high temperatures (Figure 2.2). It can
be seen that an 18% chromium stainless steel, such as Type 430 which
typically contains 0.1% combined carbon and nitrogen, is no longer
completely ferritic but transforms partially to austenite at higher
temperatures.

The formation of austenite in ferritic stainless steels when exposed
to high-temperatures thus depends on the composition of the alloy
and the rate at which it is cooled. *Nehrenbera and Lillys* (1954)
have shown that the quenching of a 17% chromium alloy which contained
austenite resulted in the formation of martensite, but that this
transformation did not occur when the chromium level was increased
to 25%. In the case of welded 17% and 21% chromium alloys, Lena et
al. (1954) found martensite in the 17% alloy and austenite in the
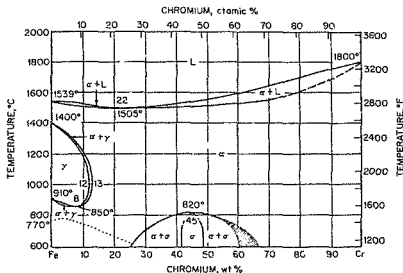21% alloy. *These results show that* untempered martensite can cause

Figure 2.1. Iron-chromium phase diagram showing the distribution of alpha, gamma and sigma phases. (From Demo, 1977).
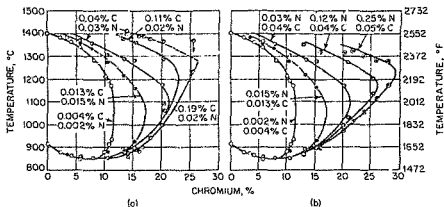

Figure 2.2. The influence of carbon and nitrogen in extending the austenite field in the iron-chromium system.
(Baerlecken et al., 1961).

embrittlement in conventional ferritic stainless steels and hence
explains the annealing practice and the need for post-weld heat
treatment in these alloys. The retention of austenite in welds is
beneficial as regards ductility but can increase susceptibility to
intergranular corrosion. Another problem associated with austenite
occurs when the alloy is heated to high temperatures and austenite
transforms to martensite by the rejection of carbon.

2.1.1. Toughness. The toughness characteristics of 18% chromium
ferritic stainless steels depend largely on the type and amount of
precipitate formed and the grain size. The effect of carbon and
nitrogen on the ductile – to – brittle transition temperature has been
examined in detail in many publications (Binder and Spendelow, 1951;
Semchyshen et al., 1971; Plumtree and Gullberg, 1974; Pollard
1974; Grubb and Wright, 1979). Early work (Krivobok, 1935) appeared
to show that notch sensitivity depended largely on the amount of
chromium present but it was shown subsequently (references above)
that interstitial elements, particularly carbon, nitrogen and oxygen,
are the controlli   ng. The significant effect of the inter-
stitial level on t   behaviour of annealed iron-chromium
alloys was only reve   when vacuum melting techniques were
developed and enabled alloys with very low interstitial levels to be
produced.

Krivobok showed that impact strength decreased sharply when the
chromium level exceeded 16% in air-melted alloys, whereas Binder
and Spendelow found that this decrease in strength in the case of
vacuum-melted alloys occurred above a chromium level of 35%. The
main reason for the difference between the air-and vacuum-melted
alloys is now known to be related to the amount of carbon and
nitrogen present. Figure 2.3, from Binder and Spendelow (1951),
shows that the carbon and nitrogen levels necessary for acceptable
room temperature impact resistance decrease significantly above a
chromium level of about 17%. The low impact resistance found by
Krivobok for alloys containing more than 16% chromium is not caused
by chromium itself but by the high interstitial levels which are
characteristic of air-melted steels.
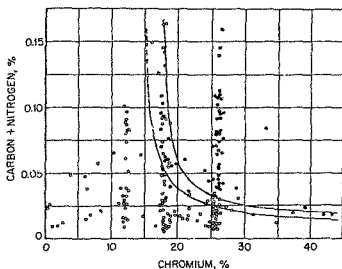
Figure 2.3. The influence of carbon and nitrogen on the toughness
of iron-chromium alloys. The plotted points represent
alloys having an impact value of 100 Joules, those
with open circles being below room temperature, those
with solid circles being above room temperature.
(Binder and Spendelow, 1951).

Another variable affecting the toughness characteristics of ferritic
stainless steels is heat treatment. The influence of heat-treatment
and the carbon and nitrogen level on the impact properties of 17%
chromium alloys is shown in Figure 2.4. The transition temperature is
found to decrease with the carbon content for both conventional
(815°C) and high-temperature (1150°C) heat-treatments although the
effect is more pronounced in the alloys that have received the high-
temperature treatment. When nitrogen is the independent variable,
the detrimental effect is evident only in those alloys that have been
subjected to the higher temperature. This effect would be significant
in welding indicating that ferritic stainless steels require closer-
interstitial control than that suggested by Binder and Spendelow (1951)
in order to have good as-welded toughness properties.
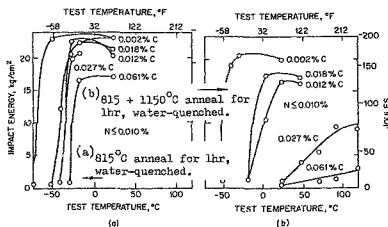
Figure 2.4. Impact transition temperature curves for quarter-size Charpy V-notch specimens of 17% chromium ferritic stainless steels as a function of carbon-content and heat treatment. (Semchyshen et al., 1971).

2.1.2. Weldability. The largest single drawback to the more wide-spread use of ferritic stainless steels is the reduction in corrosion resistance and ductility that occurs following exposure to the high-temperatures of welding. Other high-temperature effects such as 475°C and δ-phase embrittlement are less significant problems since they only occur over relatively long periods and at moderate temperatures. Unless a stainless steel has good ductility and strength (and corrosion resistance) in the as-welded condition, its application as a constructional material in the chemical process industry becomes very limited.

As in the case for toughness, the interstitial element level has a dominant effect in determining good as-welded ductility in ferritic stainless steels. Semchyshen et al. (1971) examined the effect of carbon and nitrogen on the tensile properties of autogenously welded 18Cr-2Mo stainless steel and found that carbon and nitrogen (in the combined range 50-400 ppm) had little effect on the tensile properties of the parent alloy in the annealed condition (815°C). In the case of the welded metal, however, it was found that weld ductility decreased significantly when either the carbon or nitrogen level exceeded 100 ppm. Thielsch (1951) suggested that the increase in as-welded strength with increasing interstitial content indicated that carbon and nitrogen were being taken into solution at high temperatures where they impeded plastic flow in rapidly cooled weld metal. The

various mechanisms proposed to explain the resistance to plastic
flow (Steigerwald et al., 1977) are all compatible with the fact that
ductility can be restored by annealing at temperatures (700-900°C)
which allow the agglomeration of carbides and nitrides.

Coarse grain size is only one of a number of factors contributing to
the reduced toughness of ferritic stainless steels when exposed to
high temperatures. In an investigation into the effect of composition
and heat treatment on the impact resistance of 26Cr-1Mo alloys,
Dundas (1977) found that annealing at 850°C (after a 1205°C anneal
with helium cooling) followed by water quenching lowered the transi-
tion temperature, even though the grain size did not change.
Presumably the second heat treatment caused precipitation of the
carbon and nitrogen trapped in solution when the alloy was rapidly
cooled from 1205°C.

2.1.3. Intergranular Corrosion. Another property that is influenced
by carbon and nitrogen is resistance to intergranular corrosion.
The mechanism of intergranular corrosion is the same in both ferritic
and austenitic stainless steels, namely, the precipitation of
chromium carbides and (in the case of ferritic stainless steel)
nitrides at the grain boundaries leading to local depletion of
chromium and hence decreased corrosion resistance. Precipitation can
be caused by a sensitizing heat treatment, such as occurs during the
welding process.

This type of corrosion is more of a problem in ferritic than austenitic
stainless steels because of the low solubility of carbon and nitrogen
in the ferrite lattice. The austenite lattice can retain carbon and
nitrogen in solution to relatively low temperatures so that easily
obtainable cooling rates can suppress precipitation completely.
Precipitation reactions in ferritic alloys occur at higher
temperatures and proceed so rapidly that it is very difficult to
obtain a fast enough quench to prevent precipitation.

Intergranular corrosion can be minimised or eliminated by reducing
the interstitial element level. As shown in Table 2.2, the higher the
chromium level the higher the interstitial element level that can be

accepted without initiating intergranular corrosion. It should be
noted that tolerances for weld ductility and resistance to inter-
granular corrosion vary inversely with respect to chromium level.
At low chromium levels, resistance to intergranular corrosion is the
factor determining acceptable weldability; at high chromium levels,
as-welded ductility is the limiting factor.

Table 2.2. Carbon and Nitrogen Levels Required to Produce Good
As-Welded Ductility and Corrosion Resistance in Ferritic
Stainless Steels. (Demo, 1974).

Chromium (%)	$(C + N)$ ppm Level [a]	
	For Intergranular Corrosion Resistance [b]	For Ductility [c]
19	60 – 80	700
26	100 – 130	200 – 500
30	130 – 200	80 – 100
35	250	20

(a) 2.54 mm thick sample.

(b) Intergranular corrosion resistance in boiling $Fe_2(SO_4)_3$–50% H_2SO_4.

(c) No cracking observed after bending around 5 mm rod.

From the discussion so far, it is clear that the interstitial element
level is the single most important factor to be considered in the
design of ferritic stainless steels if good toughness and weldability
is to be obtained.

2.2.   Stabilization

Since it is uneconomical, bearing in mind current stainless steel
refining technology, to lower the carbon and nitrogen levels
sufficiently to prevent the harmful effects of carbide and nitride
precipitation (a maximum combined carbon and nitrogen level of
30 ppm would be required in 19% chromium alloys), higher levels
must be accepted in practice. One method of controlling interstitial
precipitation is to add elements that are stronger in forming carbides
and nitrides than chromium, such as titanium, niobium, zirconium
and tantalum. Another method is to add low concentrations of selected
elements with atomic radii within 15% of that of the alpha matrix.
The effects of both these methods of stabilization will now be
considered.

2.2.1. <u>Titanium and Niobium Stabilization</u>. Titanium is most frequently used in the stabilization of stainless steels because it is in plentiful supply and therefore cheaper than alternatives. Niobium is sometimes preferred, although it is more expensive than titanium.

Early work by Luls et al. (1964) showed that titanium and niobium were not completely effective in preventing sensitization in alloys that had been heated to high temperatures. This was subsequently found to occur only during testing for intergranular corrosion in highly oxidizing media, and when nitrogen was not considered in the stabilization calculations. Titanium carbonitride is now known to be attacked in strongly oxidizing test solutions, such as boiling concentrated nitric acid (Bond and Lizlovs, 1969). Niobium – stabilized alloys, in contrast, are not attacked under the same conditions.

The amount of stabilization required to prevent intergranular corrosion in stainless steels varies within narrow limits (e.g. Semchyshsen et al., 1971; Wright, 1971; Pollard, 1974; Davis et al., 1980). In general, titanium additions of 6-10(C+N) are required to prevent intergranular corrosion, while for niobium the figure is 8-10 (C+N). Bond and Dundas (1973) have studied the effect of stabilization in low-interstitial chromium-molybdenum stainless steels and find that the minimum level for alloys containing 100-200 ppm carbon and the same level of nitrogen is: $Ti = 0.15 + 3.7$ (C+N). This amount of titanium is considered by the authors to be in excess of that required by stoichiometric relationships (TiC), a fact which they suggested is related to the tendency of titanium to combine with other elements in the alloy, such as sulphur. A more probable explanation relates to the fact that titanium is usually present in excess in titanium carbide (up to $Ti_{1.8}C$; Szutynski, 1979) and is therefore underestimated in assessing the composition of TiC. In the case of niobium, the amount required for stabilization is closer to stoichiometric require-ments :$Nb = 7(C+N)$.

Most studies report a linear relationship between stabilizer and carbon and nitrogen content. Also et al. (1977) found, however, that

the normal amount of stabilizer required decreases sharply below a
combined carbon plus nitrogen level of 140 ppm. According to Davis
et al. (1980), the Nb/C ratio in 26Cr-1Mo alloys is not linear and
is largely a function of the carbon level: Nb/C = 7.7 + 0.034/C. The
same authors concluded that the use of a Nb/(C+N) ratio for stabili-
zation produces misleading results since nitrogen up to 175 ppm
is not observed to affect susceptibility to intergranular corrosion.

Stabilization is necessary if intergranular corrosion in specific
environments is to be prevented, but it can have a detrimental effect
on the mechanical properties of ferritic stainless steels, especially
if present in excess of the limits noted above. Figures 2.5 and 2.6
show the effects of titanium and niobium on the impact properties of
an 18 Cr - 2 Mo alloys containing 150 ppm each of carbon and nitrogen
(Steigerwald et al.,1977). The addition of the correct amount
(0.27%) of titanium is found to increase the impact transition
temperature of the annealed alloy, as is found in the commercial
processing of ferritic stainless steels. An excess of titanium over
that required for stabilization leads to a further, slight increase
in the transition temperature. Heat-treatment of the alloy at 1205°C
to simulate welding, shows that titanium has a beneficial effect in
comparison to the unstabilized alloy.

In the case of niobium, addition of the correct amount for stabili-
zation lowers the transition temperature by about 30°C, but excess
niobium leads to an increase in the transition temperature with the
relative increase being larger than that found for excess titanium.
Niobium and titanium therefore both improve the toughness of
ferritic stainless steels that have been heated to high temperatures.

A comparison of Figures 2.5 and 2.6 shows that stabilization with
niobium has a more beneficial effect on the impact properties than
titanium. There is no obvious explanation for this difference but it
has been suggested that it is due to the different form and
distribution of the respective carbide and nitride precipitates
(Steigerwald et al.,1977). The precipitates found in niobium -
stabilized alloys are relatively small and uniformly dispersed whereas

Figure 2.5 Impact transition temperature curves for full-size,
10 mm Charpy V-notch specimens of an 18Cr-2Mo alloy
showing the effect of titanium stabilization.
(Steigerwald et al.,1977).

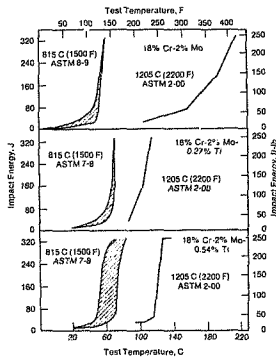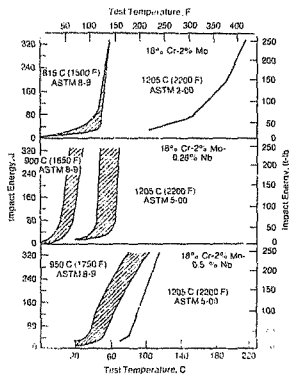Figure 9.5 Impact transition temperature curves for full-size,
10 mm Charpy V-notch specimens of an 18Cr-2Mo alloy
showing the effect of niobium stabilization.
(Steigerwald et al. (1977).

those in the titanium alloys are fairly coarse and angular.

The effect of stabilization on the properties of welded ferritic
stainless steels has been referred to briefly. Sawhill and Bond
(1976) studied the properties of autogenous welds in stabilized
18Cr-2Mo alloys and found that niobium produced a tougher weld than
titanium, with an excess of either element leading to an increase in
the transition temperature. Neither element appeared to affect the
ductility of the parent alloy over the range of stabilization
studied, 0.34 - 0.78% titanium and 0.24-0.64% niobium. It was
noted that an excess of either element reduced weld ductility, with
the effect being more pronounced in the case of niobium.

In the same study it was found that the poor weld ductility in the
alloy with excess titanium could be improved by increasing the
carbon level, indicating that the effect is dependent on the relation-
ship between titanium and the interstitial element level. The
authors considered the reduction in ductility in the alloys with
excess titanium to be due to dispersion hardening by sub-microscopic
titanium-rich precipitates. A similar explanation has been proposed
by Pollard (1974) for 26Cr-1i alloys and is supported by the fact
that a post-weld heat-treatment improves the ductility of the
alloys containing high titanium levels, possibly due to a coarsening
of the titanium-rich precipitates.

In the case of the niobium-stabilized 18Cr-2Mo alloys the poor
ductility found does not appear to be caused by the niobium-rich
precipitates. Sawhill and Bond (1976) found evidence of hot cracking
which could account for the poor ductility, a conclusion which is
supported by the fact that the ductility cannot be improved by a
post-weld heat-treatment.

The structure of the welds in superferritic stainless steels varies
according to the type of stabilization, with titanium producing
equiaxed grains and niobium a columnar structure in the centre of
the weld. The latter structure is usually observed when hot-cracking
is found to occur.

The superferritic 18Cr-2Mo alloys are affected by welding defects to
the same extent as austenitic stainless steels, but their poorer
toughness makes any defects that are present much more detrimental.
Special care must be taken to avoid undercutting or poor penetration
during welding. Gates and Jago (1982) found that marginally stabilized
18Cr-2Mo alloys (Ti = 8(C+N)) may undergo sensitization when autogenously
welded due to the formation of $M_{23}C_6$ particles. This was ascribed to
excess nitrogen combining with the titanium at high temperatures and
hence reducing the degree of stabilization in the weld metal.
Excess nitrogen could be introduced if the inert gas shielding is
interrupted in any way, or as a result of high nitrogen levels in
the filler material.

Superimposed on the effects of stabilization and interstitial level
on the ductility and impact properties of ferritic stainless steels
is the marked effect of thickness, particularly on the impact value.
The transition temperature is found to increase with material
thickness as shown in Table 2.3. High-purity alloys are known to
have higher transition temperatures when compared to alloys of
commercial purity which are stabilized with the same amount of
titanium (Steigerwald et al.,1977). This result again suggests that
uncombined titanium has a detrimental affect on the toughness
properties of ferritic stainless steels.

The evidence presented in the preceding sections shows that titanium
and niobium each have distinct advantages (and disadvantages) for the
welding of ferritic stainless steels. A combination of the two
elements therefore, seems the logical approach to producing the best
properties in a weld. Steigerwald et al. (1977) report that the best
weld ductility in an 18Cr-3Mo alloy was obtained with a combination
of 0.22% niobium and 0.1% titanium. The addition of 0.1% titanium was
found to produce a beneficial equiaxed grain structure in the centre
of the weld. However, the addition of only 0.1% titanium increased
the transition temperature of the weld relative to that of the base
alloy so that in considering the optimum niobium-titanium combination,
the titanium addition should be limited to the lowest level possible
in order to prevent the hot cracking caused by niobium.

The superferritic 18Cr-2Mo alloys are affected by welding defects to the same extent as austenitic stainless steels, but their poorer toughness makes any defects that are present much more detrimental. Special care must be taken to avoid undercutting or poor penetration during welding. Gates and Jago (1982) found that marginally stabilized 18Cr-2Mo alloys (Ti = 8(C+N)) may undergo sensitization when autogencusly welded due to the formation of $M_{23}C_6$ particles. This was ascribed to excess nitrogen combining with the titanium at high temperatures and hence reducing the degree of stabilization in the weld metal. Excess nitrogen could be introduced if the inert gas shielding is interrupted in any way, or as a result of high nitrogen levels in the filler material.

Superimposed on the effects of stabilization and interstitial level on the ductility and impact properties of ferritic stainless steels is the marked effect of thickness, particularly on the impact value. The transition temperature is found to increase with material thickness as shown in Table 2.3. High-purity alloys are known to have higher transition temperatures when compared to alloys of commercial purity which are stabilized with the same amount of titanium (Steigerwald et al.,1977). This result again suggests that uncombined titanium has a detrimental affect on the toughness properties of ferritic stainless steels.

The evidence presented in the preceding sections shows that titanium and niobium each have distinct advantages (and disadvantages) for the welding of ferritic stainless steels. A combination of the two elements therefore, seems the logical approach to producing the best properties in a weld. Steigerwald et al. (1977) report that the best weld ductility in an 18Cr-5Mo alloy was obtained with a combination of 0.22% niobium and 0.1% titanium. The addition of 0.1% titanium was found to produce a beneficial equiaxed grain structure in the centre of the weld. However, the addition of only 0.1% titanium increased the transition temperature of the weld relative to that of the base alloy so that in considering the optimum niobium-titanium combination, the titanium addition should be limited to the lowest level possible in order to prevent the hot cracking caused by niobium.

Table 2.3.   Impact Transition Temperature as a Function of Gauge
             Thickness and Titanium Level for Annealed 26Cr-1Mo
             Alloys. (Wright, 1971).

	Gauge Thickness (mm)		
	Charpy V-Notch, Transition Temperature (°C)		
C + N (%)	12.7 [a]	3.05 - 3.56 [a]	1.52 [b]
0.0065	~57	–	~73
0.0310	149	38	~73
0.0900	162	38	~18
0.300 + 0.22 Ti	121	-1	~46
0.850 + 0.45 Ti	117	38	~46

(a) Water-quenched after anneal

(b) Air-cooled after anneal

For applications where weld ductility rather than toughness is the
controlling factor, titanium is the preferred stabilizing element in
ferritic stainless steels. Such applications include most of those
involving light gauge products (4mm or less) which covers the main
use of stainless steel.

While titanium appears to be the preferred stabilizer in commercial
18Cr-2Mo superferritic stainless steels either alone (e.g.Nyby ELI-T
18 and 18-2, MONIT and Famsteel 18-2), or in combination with niobium
(e.g.Type 444 ; Table 2.1), other element combinations are used, such
as niobium and tantalum in the equivalent Japanese grades.

To summarize, the addition of the optimum amount of a stabilizing
element to an alloy containing a moderate amount of carbon and
nitrogen (e.g. 400 ppm combined) does not improve the annealed impact
properties but will significantly improve the as-welded ductility and
corrosion resistance. This point is an important difference between
stabilized and low-interstitial alloys and as shown by Wright (1971),
is particularly evident at section thicknesses greater than 3 mm
(Table 2.3). For thick plate sections where high room-temperature
toughness is required, the low-interstitial alloys, but not the

stabilized alloys, would be acceptable. On the other hand for thin
material, as used in heat exchanger tubing, either alloy could be
used because both have similar toughness and welded properties.

2.2.2.   Stabilizing Alloy Additions.   An alternative method of
reducing the deleterious effects of carbon and nitrogen in ferritic
stainless steels, apart from reducing carbon and nitrogen to very low
levels or adding titanium and niobium as stabilizers, is the use of
low concentrations of elements having atomic radii within 15% of that
of the alpha matrix. Sipos et al. (1972) have shown that good as-
welded ductility and intergranular corrosion resistance can be
produced in 25-37% chromium ferritic steels containing 250 ppm
combined carbon and nitrogen by the addition of 0,1-1% of selected
elements such as aluminium or copper, or combinations of aluminium
and copper;   aluminium and vanadium;   and aluminium, copper and
vanadium. An alloy with a moderate interstitial element level and
containing these elements as stabilizers can be produced more
economically than one of equivalent weldability containing a very
low interstitial level.

Vanadium has been cons.. ered as a stabilizer in stainless steel in
several publications and reports (Aslund,1977;   Krupp patent;
Scurr, 1978) and this aspect is discussed further in the section on
vanadium (3.1.3).

2.3.   Embrittling Effects

Ferritic stainless steels cannot be strengthened or hardened by the
classical gamma-martensite transformation but are susceptible to
significant strengthening by heat treatment. A drawback to any heat
treatment is the occurrence of embrittling phases which can cause a
loss of ductility and toughness at room temperature. Several
embrittling phenomena have been identified in stainless steels
including sigma and chi phase precipitation, 475°C embrittlement and
high-temperature embrittlement. The last of these is particularly
serious since ferritic stainless steels must have good ductility,
toughness and corrosion resistance after welding if they are to find
more widespread application.

2.3.1. Sigma and Chi Phase Precipitation. The chromium concentration
and upper temperature range in which sigma phase occurs is shown in
the iron-chromium diagram (Figure 2.7). Pure sigma forms in the
chromium range 42-50% while a duplex structure comprised of alpha and
sigma phases is found in alloys with as little as 9.5% chromium when
they are exposed to temperatures as low as 482°C. Sigma phase is a
hard, brittle, inter-metallic compound that forms congruently from
ferrite at 815°C, and has the nominal composition FeCr. The relation-
ship between sigma and alpha prime (Figure 2.7) is not clear but there
is evidence to suggest that alpha prime is a precursor of sigma at
temperatures below 560°C (Steigerwald et al.,1977).
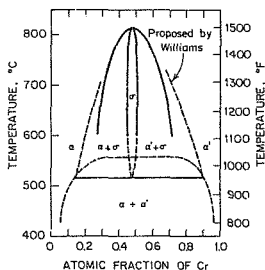

Figure 2.7.   Temperature range for stable sigma and
                metastable alpha prime phases in the
                iron-chromium system. (Williams, 1958).

The amount of sigma phase present in ferritic alloys depends on
factors such as cold work and the presence of certain other elements.
Cold work is found to accelerate the precipitation of sigma phase.
Ferrite stabilizing elements such as molybdenum, silicon, vanadium,
titanium and niobium which dissolve in the sigma phase, lead to more
rapid formation and to an extension of the temperature range over
which sigma phase is stable. The effect of carbon is to decrease
sigma formation, this being attributed to the removal of chromium
from solid-solution by the formation of chromium carbide.

The most significant effect of sigma formation on the room temperature
properties of ferritic stainless steels is to raise the impact
transition temperature; the effect on other mechanical properties
is not so marked although hardness is increased and ductility
reduced. At high temperatures sigma could of course have a beneficial
effect by increasing the tensile strength. As regards corrosion
resistance, large sigma particles are not found to have much effect.
When sigma occurs as a fine grain-boundary precipitate, however, the
corrosion resistance is adversely affected as shown by tests in aqua
regia (Newell, 1946) and nitric and sulphuric acids (Cooke, 1950).

The precipitation of sigma phase is very slow and it is not normally
encountered in the processing of commercial ferritic stainless steels.
Shortsleeve and Nicholson (1951) have shown that sigma takes some
500 hours to form in 18% chromium stainless steels at 595°C, so
that it is not expected to occur in weld deposits. Long isothermal
holds are therefore necessary for sigma phase to significantly
affect the ductility and toughness of ferritic stainless steels.

As regards the practical application of ferritic stainless steel as a
heat resistant material, sigma phase is only a limiting factor for
use in the temperature range 500-815°C for long periods. It is
important therefore in developing new stainless steels to consider
the effect of composition on sigma formation in relation to their
final application. Any sigma phase that does form can be dissolved
by annealing at over 815°C for one hour. Alloys containing elements
such as molybdenum, nickel and manganese will require longer annealing

periods or higher temperatures to dissolve sigma phase.

Another intermetallic compound which is closely related to sigma and is found in molybdenum-containing ferritic stainless steels, is the chi-phase. It has the nominal composition Fe_2CrMo. Research shows that chi appears faster than sigma, and that both generally occur together in molybdenum-containing stainless steels (Steigerwald et al.,1977). In an 18Cr-2Mo alloy with a combined carbon and nitrogen content of 300 ppm, chi phase forms in 300 hours at 750°C. Increasing the molybdenum content and the temperature considerably reduces the time for chi to form. As is to be expected, chi phase reduces the notch toughness of molybdenum-bearing, ferritic stainless steels. Since chi is stable over a wider temperature range than sigma, annealing at around 980°C is needed to eliminate it in alloys with 18% chromium and over 3.5% molybdenum (Schmidt and Jarleborg, 1974).

2.3.2.   475°C Embrittlement. When ferritic stainless steels are heated for extended periods in the temperature range 320 - 550°C, they undergo hardening and a marked reduction in ductility and toughness. This embrittlement effect occurs most rapidly at 475°C and is caused by the precipitation of very fine chromium-rich particles called alpha prime (Figure 2.7). These precipitates, which have a maximum diameter of a few hundred Angstroms, appear to cause a reduction in toughness and ductility by the immobilisation of dislocations. The precipitation of alpha prime is, however, a reversible process and can be removed by annealing at temperatures above 550°C.

475°C embrittlement is very sensitive to the amount of chromium present and is also very temperature dependent. A 13% chromium ferritic stainless steel is embrittled in 65000 hours, whereas a 15% chromium alloy takes only 700 hours. The most marked effect of alpha prime precipitation is reflected in an increase in the impact transition temperature. For example, a 17% chromium alloy (with 800 ppm carbon) has its impact value reduced from 12 to 4 kg/cm^2 after being exposed to a temperature of 450°C for 4 hrs. At higher chromium levels (25 - 30%) the embrittlement is further accentuated. Although the embrittled alloy has very poor room-temperature impact

properties, it would probably have reasonable toughness at the
service temperature that caused the embrittlement initially and in
consequence 475°C embrittlement is only a problem as far as mechanical
properties are concerned when room temperature toughness is of
importance. When this is the case, ferritic stainless steels
containing more than 15% chromium should not be exposed to temperatures
above 320°C.

Apart from chromium, other elements such as titanium, niobium,
molybdenum, carbon and nitrogen enhance the embrittling effect in
ferritic stainless steels (Table 2.4). The effect of interstitial
elements is probably related to the interaction between alpha prime
and carbonitride precipitates and it has been suggested that they may
even reduce embrittlement by immobilizing part of the chromium
(Mediratta and Ramaswamy,1976). Some elements such as aluminium,
nickel, silicon and manganese have been shown to slow down the
embrittlement in 18Cr-2Mo stainless steels, with silicon and manganese
being the most promising in this respect (Grubner, 1973). The
addition of these alloying elements is not, however, significant
enough to affect the practical applications of ferritic stainless
steels.

In addition to affecting the mechanical properties, 475°C embrittle-
ment has a detrimental effect on corrosion resistance. Newell (1946)
has shown that an embrittled 27% chromium alloy corrodes from 4 to
12 times more rapidly in boiling concentrated nitric acid, than does
the annealed alloy. This accelerated corrosion is probably a result
of selective attack of the iron-rich alpha prime phase or, as
suggested by Hodges (1971), to attack of chromium-rich carbide
precipitates. Lizlovs and Bond (1975) found that 475°C embrittlement
reduces the corrosion resistance of 18Cr-2Mo-Ti stainless steels in
a variety of environments, including those which are oxidising/reduc-
ing, and under pitting conditions. 475°C embrittlement affects
corrosion resistance much more slowly than it does the toughness
properties so that if the steel is satisfactory as far as mechanical
properties are concerned, it will be acceptable from a corrosion
point of view.

2.4. The Effect of Composition on 475°C Embrittlement
in Ferritic Stainless Steels

Element	Effect on 475°C Embrittlement
Cr	intensifies
C	no effect[a]; intensifies[b]
Ti, Nb	intensifies
Mn	lowers slightly
Si	intensifies
Al	intensifies
Ni	low amounts intensify
	large amounts decrease
N	very slight[a]; intensifies[b]
P	intensifies
Mo	intensifies
V	variable[c]
severe cold work	intensifies[d]

(a) Heger, 1951.
(b) Grobner, 1973
(c) Miwa et al., 1968.
(d) Thielsch, 1951

The rate of formation of alpha prime is slow and does not cause
problems in the processing of ferritic stainless steels. Cold work
is known to increase the rate of embrittlement. As with sigma phase,
welding or a high-temperature heat-treatment is unlikely to produce
475°C embrittlement, even in situations where relatively slow cooling
through the embrittling temperature range occurs. However, ferritic
stainless steels with more than 16% chromium should not be used for
extended service between 370 and 530°C, especially if the alloy is
cycled from room temperature to the operating temperature during
process shut-downs or temperature excursions.

2.3.3. High-temperature Embrittlement. When ferritic stainless
steels with more than about 16% chromium are heated above 950°C and
cooled to room temperature, they become embrittled (show a loss of

toughness and ductility) and susceptible to intergranular corrosion. These effects, which have been briefly referred to in a previous section on the rôle of carbon and nitrogen, can occur during welding, isothermal heat-treatments above 950°C, and casting processes. As a result, high-temperature embrittlement has limited the more extensive use of air-melted ferritic stainless steels.

It is generally agreed that this form of embrittlement is due to the detrimental effects of chromium carbides and nitrides, and is related to the chromium and interstitial element levels present in the alloys, as well as to the rate of cooling. Baerlecken et al. (1961) studied the effect of chromium in vacuum-melted ferritic stainless steels and found that the loss of toughness due to a high-temperature heat-treatment in alloys subsequently air-cooled increased with chromium level. The effect was found to be very small at the 16% chromium level. The authors ascribed the embrittlement to the fact that chromium leads to an increase in the amount of carbides and nitrides formed. The same alloy, however, when reheated to 1050°C and water-quenched showed good toughness due to suppression of carbide and nitride precipitation. Another important conclusion from the work of Baerlecken et al. is that grain size has little effect on notch impact behaviour in high-purity alloys. Demo (1977) examined the effect of cooling rate after a high-temperature heat-treatment (1100°C) in conventional and high-purity (combined carbon and nitrogen of 180 ppm) ferritic stainless steels and found that water quenching of the commercial stainless steel (Type 446) produced a marked loss of ductility (elongation) although air cooling did not. No loss of ductility was noted when the high-purity alloys were either air-or water-cooled.

Demo (1977) and Baerlecken et al. (1961), and Semchyshen et al. (1971) interpret their results in different ways, the first two authors considering grain matrix precipitation to be the major cause of the embrittlement whereas Semchyshen et al. relate it to grain boundary precipitation. These three authors agree, however, that carbide and nitride precipitation is the cause of the embrittlement and that it is very dependent on the levels of carbon and nitrogen present.

It would appear that the same precipitation mechanism causing this form of embrittlement is also responsible for the loss of corrosion resistance found when ferritic stainless steels are heated to high temperatures. The effects of high-temperature embrittlement can be reduced by heating the alloy in the temperature range 750 to 850°C, followed by rapid cooling.

2.4. Cooling Rate

The toughness and ductility of ferritic stainless steels can be affected by the rate at which cooling occurs from elevated service temperatures, as already discussed in connection with welding and high-temperature embrittlement. The rate at which cooling occurs during fabrication can also significantly affect these properties.

The optimum toughness properties in low interstitial ferritic stainless steels are produced by rapid cooling from the annealing temperature range of 750 - 900°C. This is due to the fact that rapid cooling suppresses the precipitation of carbides and nitrides and delays the onset of 475 °C embrittlement. In stabilized alloys, work by Climax Molybdenum (Steigerwald et al.,1977) on the post-weld heat-treatment of stabilized 18Cr-2Mo alloys stainless steel indicates that rapid cooling is more beneficial than slow cooling. Although the precipitation of chromium carbides and nitrides is not expected in these alloys, Grobner (1973) has found evidence for such reactions and this may be the reason why rapid cooling is more beneficial.

Most of the reactions involving the precipitation of detrimental intermetallic compounds occur slowly and are therefore not expected to influence the processing of ferritic stainless steels under conventional fabrication conditions. It should be remembered, however, that certain alloying elements increase the rate of precipitation reactions and if present in sufficient amounts may become important during fabrication. As a result, the slow cooling of superferritic stainless steels in the range 300 - 850°C should be avoided and is the reason why rapid cooling is preferred in contrast to the long isothermal anneal used for Type 430.

3. EFFECT OF VANADIUM AND OTHER ELEMENTS ON THE
MECHANICAL PROPERTIES OF FERRITIC STAINLESS
STEELS

The effects of the alloying elements molybdenum, titanium and niobium
have been described in some detail in the previous section and will not
be considered here. To summarize, molybdenum up to 2 to 3% has very
little influence on the mechanic ' properties of stainless steel ,
being present largely to improve the corrosion resistance. In excess
of 3 to 4%, however, molybdenum reduces the toughness of ferritic
stainless steels due to the formation of embrittling phases. Titanium
and niobium are present in low concentrations in stainless steels as
stabilizers to combine with carbon and nitrogen, thus preventing the
precipitation of chromium carbides which lead to intergranular
corrosion. Under normal processing conditions in 18Cr-2Mo alloys
(anneal at 815°C following by water quenching), titanium raises the
impact transition temperature, but niobium lowers this temperature.
Niobium has the detrimental effect of causing hot-cracking in stainless
steels. Both elements, when present in the correct amounts, improve
the toughness of ferritic stainless steels which have been heated
to a high temperature, as in welding.

3.1. Vanadium

Vanadium has been considered as an alloying element in 11-12% chromium
steels and in austenitic stainless steels largely from the point of
view of improving the creep-rupture properties. A very limited amount
of research has been carried out on ferritic stainless steels where
the effect of vanadium on the tensile and impact properties, on 475°C
embrittlement and as a stabilizer has been investigated.

The largest use of vanadium is as an alloy element in high-strength low-
alloy steels where it combines with carbon to form hard, stable carbides.
These are always minute and evenly dispersed and have a considerable
influence on the grain size of the steel. It has been shown that
small quantities of vanadium inhibit the tendency of chromium carbides
to agglomerate. Vanadium thus has a considerable effect on the
ductility, fatigue strength and notch sensitivity of high-tensile

chromium and chromium-tungsten steels which are very deficient in
those properties.

3.1.1.   Carbides and Nitrides Formed. The solubility of carbon and
nitrogen in ferrite is some ten times lower than in austenite at room
temperature. Because of this low solubility, almost all the carbon and
nitrogen in ferritic stainless steels are present in the form of
precipitates at room temperature in slowly cooled alloys. The
dominant carbide in conventional ferritic stainless steels is the
$M_{23}C_6$ type, with M representing mostly chromium, and the remainder
being iron. In the presence of other carbide formers, $M_{23}C_6$ is often
found in combination with other carbides, and chromium is partially
replaced by the incoming elements e.g. $(Cr, Fe, Mo)_{23}C_6$. Nitrogen is
largely present as Cr_2N in Fe-Cr stainless steels.

The carbides and nitrides formed in ferritic stainless steels can be
dissolved by heating above about 850°C, with nitride going into
solution faster than the carbide. On slow cooling from solution
temperatures the carbide precipitates first, this precipitation
occurring preferentially at the grain boundaries. As a consequence,
intergranular corrosion is closely related to grain boundary carbide
precipitation. The nitride precipitates occur along the grain
boundaries only when the carbon content is very low. Precipitation
of carbides and nitrides can be suppressed in ferritic stainless steels
by rapid quenching only in the case of very low carbon and nitrogen
contents.

Other forms of carbide precipitation in addition to the $M_{23}C_6$ type ,
such as MC, can occur when strong stabilizing elements are present
(e.g. titanium, niobium and vanadium). MC carbides usually precipitate
intragranularly, although under some conditions precipitation at
grain boundaries can occur. Vanadium is known to occur as V_4C_3 in
austenitic stainless steels and usually precipitates on dislocations
and stacking faults, somewhat similar to MC carbides (Novak, 1977).

An essential difference between molybdenum and vanadium is that
 dybdenum remains largely in solid-solution whereas vanadium occurs
both in solid-solution and as a precipitate. Under conditions of

slow cooling molybdenum can occur as a precipitate, usually the kappa carbide $(FeCrMo)_{23}C_6$, or can form intermetallic compounds such as the sigma and chi phases under certain temperature conditions. Vanadium is a stronger nitride and carbide former than molybdenum (molybdenum is a particularly weak nitride former) and therefore precipitates as both carbide (usually V_4C_3) and nitride (VN) under suitable conditions. The mechanics of vanadium nitride formation in stainless steels have not been discussed in as much detail in the literature as for vanadium carbide, because carbide formation is the required strengthening mechanism for creep resistance. The nitride forming properties of vanadium, however, are used in low-alloy high-strength steels where the nitride produces a fine ferrite grain size and occurs as a carbide or carbonitride precipitate in the ferrite (Sage, 1976). In austenitic stainless steels, small additions of vanadium (0.5%) produce creep-induced precipitation of VN_{1-x} in the matrix and on dislocations.

The thermodynamic stability of various alloy element carbides and nitrides has important consequences for their choice as stabilizers in stainless steels (Figure 3.1). The relative position of vanadium in this figure is important in the interpretation of the different precipitates to be expected in stainless steels.

The author is not aware of any work on phase-fields in the iron – 18% chromium-vanadium-carbon system. The Fe-Cr-V system has been examined by Martens and Duwez (1952) who constructed a single iso-thermal section at 700°C (Figure 3.2). Sigma phase is found to be continuous across the figure. The iron corner of the Fe-V-C system is shown in Figure 3.3. The proportion of V_4C_3 is seen to increase as the carbon level drops, to the extent that below about 0.03% carbon, vanadium is completely soluble in ferrite and no carbide is formed.
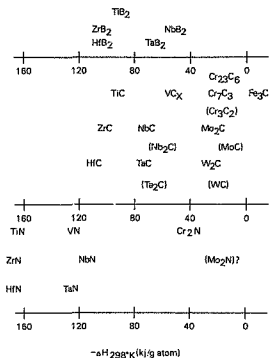
Figure 3.1 Enthalpies of formation of various
carbides and nitrides.(Schick, 1966).
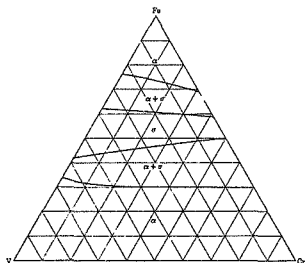
Fig. 3.11. Isothermal section at 700°C for the system V-Fe-Cr.

Figure 3.2. Isothermal section at 700°C for the
Fe-Cr-V system.(Martens and Duwez, 1952).
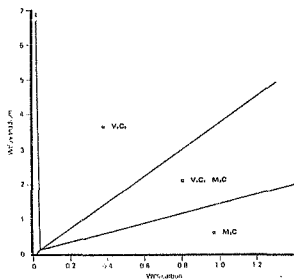
Figure 3.3. Constitution diagram for the Fe-V-C system at
700°C.(Woodhead and Quarrell, 1965).

Rostocker (1958) considers that vanadium does not function as a carbide former in 10-12% chromium ferritic steels, being present largely in the ferrite with chromium forming chromium carbide. Detailed work by Shaw and Quarrell (1957), however, shows that vanadium carbides do in fact form at higher vanadium levels (Figure 5.4).

Figure 5.4. Carbide constitution diagram at 700°C for the Fe-Cr-V-0.25% system. (Shaw and Quarrell, 1957).

Rostocker (1958) considers that vanadium does not function as a carbide former in 10-12% chromium ferritic steels, being present largely in the ferrite with chromium forming chromium carbide. Detailed work by Shaw and Quarrell (1957), however, shows that vanadium carbides do in fact form at higher vanadium levels (Figure 3.4).

Figure 3.4. Carbide constitution diagram at 780°C for the Fe-Cr-V-C system. (Shaw and Quarrell, 1957).

Publications which have examined the effect of vanadium on the ageing
behaviour of stainless steels with carbon contents of 0.1 to 0.2% are
Odesskii et al.(1978) and Argent et al. (1970) (ferritic alloys), and
Silcock (1973), Shinoda et al. (1973), Irvine et al. (1961), Irani and
Weiner (1965) and Borggreen and Tholen (1976) (austenitic alloys).
Odesskii et al. found that the addition of titanium and vanadium
(1-1.5%) to a 17% chromium alloy containing 0.1% carbon completely
suppressed the alpha to gamma transformation at the grain boundaries,
thus improving ductility. Microprobe examination revealed that
titanium occurs as stable carbides while vanadium is found mainly in
alpha solid-solution. The only publication which has examined low
carbon and nitrogen levels more in line with those of the present study
is that of Irani and Weiner (1965). In the ageing at 600-900°C of a
20Cr-25Ni stainless steel containing 4.5% vanadium and two carbon
levels, 0.02 and 0.15%, the equilibrium precipitate was a Cr-V-Fe
sigma phase. In the alloy with the higher carbon level, sigma
phase was preceded by the precipitation of vanadium carbide, V_4C_3.

To summarize, vanadium occurs both as a precipitate and in solid-
solution in stainless steels. In the ageing of stainless steels with
moderate carbon and high vanadium (over 2%) levels, vanadium is found
to restrict the formation of the $M_{23}C_6$ phase in addition to stabilizing
it in a finely divided form presumably because vanadium retards the
diffusion of chromium in the ferrite, a process which must take place
if coarsening of the carbide is to occur. In low carbon (100 ppm)
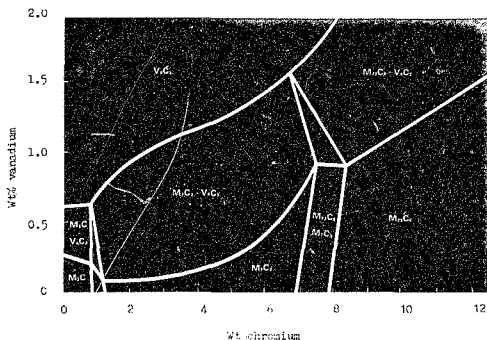ferritic stainless steels processed in the normal way (short anneal
at 850°C followed by water quenching) much of the vanadium is expected
to remain in solid-solution and any vanadium that does precipitate
would first do so as a nitride or carbonitride and only subsequently
enter into the Cr-V-Fe sigma phase, and other carbide phases.

3.1.2.   Mechanical Properties. The author is aware of only four
sources of information relating to the effect of vanadium on the tensile
and toughness properties of ferritic stainless steels, these being
unpublished data by Climax Molybdenum and Middelburg Steel and Alloys
(South Africa) (Scurr, 1978),and papers by Sipos et al. (1972) and
Aslund (1977). Climax Molybdenum determined the effect of up to 3%
vanadium in 18-24% chromium stainless steels with a combined carbon

and nitrogen level of 300 ppm. The tensile properties and impact
transition temperature for the alloys are shown in Table 3.1, and shown
for comparison in Table 3.2 are the same properties for the alloys
containing molybdenum. A comparison of these tables shows that
vanadium has two very beneficial effects when compared to molybdenum:
it lowers the impact transition temperature and produces good ductility
in the as-welded condition. Climax Molybdenum have suggested that
these results are due to the improved grain refining properties of
vanadium compared to molybdenum. The tensile strengths for both
sets of alloys of the same alloy content are similar, although the
values in the case of molybdenum are all slightly higher.

Aslund (1977) examined the effect of 1.1% vanadium in Type 444 stain-
less steel mainly from the point of view of stabilization. Table 3.3
shows that vanadium lowers the impact transition temperature, thus
confirming the result of Climax Molybdenum.

Midd lburg Steel and Alloys (Scurr, 1978) have carried out a
preliminary investigation into the use of vanadium in 12Cr-0.03C alloys.
It was concluded that vanadium at a level of 6(C+N) has a beneficial
effect on the impact strength of the annealed, titanium-free steel.
Vanadium was not found to be as effective as titanium in retarding
the loss of impact strength suffered by the steel after a high-
temperature heat-treatment. There were indications, however, that
higher vanadium levels are more effective in this regard, and it was
suggested that a mixed stabilization consisting of low titanium and
high vanadium levels may show promise.

Vanadium is found to have a beneficial effect on the as-welded
ductility and corrosion resistance of 28-36% chromium stainless steels.
Sipos et al. (1972) report that the addition of up to 1.3% of vanadium
(or other elements, such as copper) had the same effect on these
properties as a low interstitial level of 15 ppm.

3.1.3. Stabilization. Vanadium can be used as a stabilizer because
it is a strong carbide and nitride former. However, because it occurs
both in solid-solution and as a precipitate, a higher vanadium level

Table 3.1.   Mechanical Properties of Vanadium-Bearing Superferritic Stainless Steels (Unpublished Data, Climax Molybdenum)

Nominal Composition (a)	Heat Treatment	CVN 50% Shear Transition Temp. (°C)	Yield Strength (MPa)	Ultimate Strength (MPa)	% Elongation
18Cr - 1V	816°C 1 Hr WQ 1204°C 15 Min He Cool	-46	237	408	38.0
	TIG Weld	121	309	423	21.2
18Cr - 2V	816°C 1 Hr WQ 1204°C 15 Min He Cool	16	250	423	38.0
	TIG Weld		259	421	25.7
18Cr - 3V	816°C 1 Hr WQ 1204°C 15 Min He Cool	-34	254	433	35.2
	TIG Weld	29	272	446	30.0
18Cr - 3V	816°C 1 Hr WQ 1204°C 15 Min He Cool	71	242	445	35.0
	TIG Weld	116	279	447	28.0
24Cr - 1V	816°C 1 Hr WQ 1204°C 15 Min He Cool	-23	289	457	33.0
	TIG Weld	154	365	478	20.0
24Cr - 2V	816°C 1 Hr WQ 1204°C 15 Min He Cool	16	294	472	32.0
	TIG Weld	65	327	479	23.5

(a) $C + N = 0.03\%$

Table 3.2   Mechanical Properties of Molybdenum-Bearing Superferritic Stainless Steels (Unpublished Data, Climax Molybdenum)

Nominal Composition	Heat Treatment	CVN 50% Shear Transition Temp. (°C)	Yield Strength (MPA)	Ultimate Strength (MPA)	% Elongation
18Cr-2Mo-.008C - .019N	816°C 1 Hr WQ 1204°C 1 Hr WQ TIG Weld	160	281 431	451 533	30.5 7.5
19Cr-1.8Mo .015C - .010N .11Ti(a)	816°C 1 Hr WQ 1204°C 1 Hr WQ TIG Weld	127	288 372	469 510	34 10.7
18Cr-1.6Mo .018C - .009N- .26Ti	1204°C 1 Hr WQ	82			
18Cr-2Mo- .034C - .005N- .47Ti	816°C 1 Hr WQ TIG Weld		270 301	462 475	.1 .1
26Cr-1Mo .012C - .02CN	°C 1 Hr WQ	10			
26Cr-2Mo- .011C - .009N	°C 1 Hr WQ	21			

(a) Heat not stabilized in welded condition

Table 3.3.   Effect of Stabilization with Vanadium and
other Elements on the Impact Properties of
18Cr-2Mo Ferritic Stainless Steels[a] (Aslund, 1977).

Stabilizer	%	Transition Temperature (°C)[b]	Shelf Energy J/cm²
Nb	5	+ 20	200
Zr	0.5	+ 95	120
Nb+Al	0.3+0.2	+ 5	280
V	1.10	– 10	220
V+Ti	1.10	+ 65	180

[a]   5 mm sheet, hot rolled and water quenched. C + N = 250 ppm

[b]   Minimum temperature for 35 J/cm²
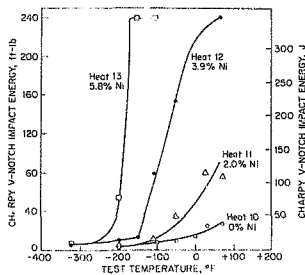
Figure 3.5.   The effect of nickel on the impact toughness of
vacuum-melted 25% chromium stainless steels containing
300 ppm carbon.   Full-size, 10 mm Charpy V-notch
specimens used.   (Floreen and Hayden, 1968).

is required to give the same degree of stabilization as titanium or
niobium. Titanium and niobium precipitates are stable to higher
temperatures than those of vanadium which form in the temperature
range 650-800°C. Annealing an Fe-Cr-V alloy at 850°C for a short
period followed by water quenching, would result in the dissolution of
a large percentage of the vanadium precipitates. Since titanium (and
niobium) precipitates are stable at high temperatures (over 1000°C)
annealing an Fe-Cr-V-Ti alloy under the same conditions would not
dissolve these precipitates. A certain amount of vanadium may be
present in the high temperature precipitates because vanadium forms a
continuous solid-solution series with titanium or niobium.

Vanadium is not present as a stabilizer in commercially produced
stainless steels. Defilippi and Rutz (1974) patented a martensitic
stainless steel utilizing vanadium instead of titanium as the carbide
former. Because the carbides and nitrides of vanadium are more
soluble in stainless steel than those of titanium, more carbon and
nitrogen is available during solidification to prevent the formation
of delta ferrite in turn reducing the amount of nickel necessary
for this purpose.

The use of vanadium as a stabilizer has been referred to in the previous
section (3.1.2.). According to Aslund (1977), vanadium shows promise
as a stabilizer in an 18Cr-2Mn-1.1V stainless steel but has the draw-
back that it does not prevent intergranular corrosion.

3].4.   475°C Embrittlement. Strong carbide formers (e.g. titanium
and niobium) are known to increase the rate of 475°C embrittlement
(table 2.4.). Vanadium, however, is reported to have a beneficial
effect in decreasing this embrittlement (Mima et al.,1968). This
result has been confirmed by Koutaniemi et al. (1974) in titanium-
stabilized 17% chromium stainless steels but only above a vanadium
concentration of about 1.5%. Up to 1.2%,vanadium actually increased
the rate of age-hardening at 475°C, an effect which was ascribed to
vanadium substituting for iron or chromium in the precipitating phase
or increasing the amount of this phase.

3.2. Nickel

3.2.1. Mechanical Properties. Nickel is well known to have a
beneficial effect on the mechanical properties of ferritic stainless
steels (in particular on the impact transition temperature) in
addition to improving general corrosion resistance. One of the reasons
it is not added to ferritic stainless steels (in small amounts) is that
it causes susceptibility to stress-corrosion cracking, especially in
the presence of molybdenum.

Research on the effect of nickel has concentrated on the high-chromium
ferritic steels (25% chromium) because they can dissolve more nickel
in the matrix without forming austenite. The presence of austenite,
however, can have a beneficial effect on the impact propeties as shown
by Floreen and Hayden (1968). Figure 3.5 illustrates the marked
effect of nickel in low-interstitial, 25% chromium ferritic stainless
steels. The impact transition temperature was found to be lowered to
a greater degree than expected, a feature which the authors suggested
might be caused by the effect of nickel in reducing the extent of the
embrittling reaction during cooling.

*Other publications which have noted the effect of nickel in improving
toughness are those by Okada et al. (1975), Brandis et al. (1977),
Bond et al. (1977) and Aslund (1977). Okada et al. and Bond et al.
showed that the effect of nickel on the impact transition temperature of
25 to 28% chromium - molybdenum alloys depended on the rate of
cooling, with rapid cooling producing a lower transition temperature.
In the work of Bond et al., nickel was found to be beneficial above a
concentration of 2% in 25 Cr - Mo - 0.01C alloys, with 4% nickel
lowering the impact transition temperature by 180°C compared to the
nickel-free alloy.*

Regarding the effect on the tensile properties, Aslund (1977) found
that 4% nickel increased the yield strength and decreased the
elongation (from 25 to 20%) in a 25% chromium stainless steel. Nickel
also had a strong influence on the mechanical properties after welding.
Snape (1977) noted that 2.5% nickel increased the yield strength
from 331 to 448 MPa in electron-beam melted 26Cr - 1Mo alloys .

The use of nickel in promoting intermetallic compound precipitation in ferritic stainless steels, thus leading to age-hardening, has been referred to by Snape (1977). Intermetallic compound precipitation can be avoided by annealing at temperatures above 1000°C.

3.2.2.   Weldability.   According to Arness (1943), the addition of 0.3 to 3% nickel to alloys containing 8-15% chromium and less than 0.07% carbon produces strong, tough welds characterised by a fine-grained structure. For applications where stress-relieving is impractical, Arness recommends an optimum nickel level of 1%.

Nickel is reported to reduce the toughness of 25% chromium alloys slightly after prolonged exposure at 704°C, a feature attributed to sigma formation (Eberle, in Snape, 1977).

3.3.   Silicon
Silicon is a ferrite-forming element in the iron-carbon system and its effect on the mechanical properties of ferritic stainless steels is analagous to chromium: tensile strength and yield values are raised at the expense of ductility. It also has the somewhat detri- mental effect of increasing the tendency for grain growth at elevated temperatures. For applications where toughness and impact strength are required, high silicon appears to be quite detrimental and should not exceed about 0.8% in conventional ferritic stainless steels. The net effect in stabilized alloys is to raise the average impact transition temperature by up to 60°C for every 1% of silicon added (Thum, 1935). The two main benefits of adding silicon to ferritic stainless steels are in improved resistance to pitting corrosion and to high-temperature scaling and oxidation.

The addition of silicon to stainless steels has the particularly detrimental effect of increasing both the rate of formation and upper temperature limit, as well as the range of formation, of sigma phase. In alloys containing 30 – 35% chromium, not more than 1.5 – 2% silicon should be added if adequate ductility is to be retained in the wrought condition, but in the case of cast alloys more silicon can be

added. For applications where sigma formation can have a detrimental effect, for example in thick sections, the silicon level should not exceed 0.5 to 0.75% (Bieber, 1975).

In the development of a more corrosion-resistant Type 316 stainless steel, Streicher (1956) found that an upper limit of 2.5% silicon was necessary because of problems encountered during processing of the alloy.

3.4. Copper

Copper does not form carbides but occurs in solid-solution in stainless steels, being soluble in ferrite to the extent of 1.4%. The presence of copper affects the properties in three ways: corrosion resistance, response to heat-treatment, and tensile properties. The optimum level of copper with respect to each of these properties is about 1%, regardless of the chromium content (Thum, 1935).

The most noticeable effect of a 1% copper addition to a 13% Cr-0.16%C steel is to raise the elastic limit. It is also found that there is a slight increase in elongation while the impact strength is decreased slightly (Thum, 1935).

Sandomirskii (1978) examined the effect of ageing on the mechanical properties of a 1%Cr - 1Mo - 0.3V - 1.6Cu - 0.06C steel. Ageing at 600°C for 100 hours improved both the tensile strength and fracture toughness values. The effect of copper was to reduce the amount of carbide phase as well as promote the saturation (and stability) of $M_{23}C_6$ carbides with chromium.

Copper is reported to retard grain growth in ferritic stainless steels at elevated temperature (Thum, 1935). A 1% copper addition requires a 10 to 55°C temperature increase to produce the same hardness and tensile strength compared to the alloy without copper.

4. THE EFFECT OF VANADIUM AND OTHER ELEMENTS ON THE CORROSION RESISTANCE OF FERRITIC STAINLESS STEELS

The base alloy employed in this study is one containing 18% chromium since this figure appears to be an optimum from an economic, fabrication and corrosion resistance point of view, and it is the base composition of the most widely used superferritic stainless steel. Other elements apart from vanadium and molybdenum, which are considered to have potential beneficial effects on corrosion resistance in ferritic stainless steels are silicon, nickel and copper. The effects of these various elements will be considered in detail in this section.

Fundamental to the corrosion resistance of a stainless steel is the ability to passivate in a particular environment, that is, to remain chemically inactive as a result of the formation of a passive oxide film. Although little is known about the mechanism of passivity, the phenomenon is well documented and provides the basis for selecting an element or alloy combination for use in a corrosive situation. Since passivity is such an important aspect of corrosion resistance, it will be discussed at length.

4.1. Passivation of Stainless Steels

4.1.1. Anodic Polarization and Passivation. The study of anodic polarization is at present the most widely used approach for developing new stainless steels that are passive. As a general rule, the introduction of an easily passivated element into an alloy causes the alloy to adopt to a greater or lesser extent the passive properties of the introduced element. The magnitude of this effect in a given situation may depend additionally on the operation of synergistic processes.

In discussing the influence of alloying elements it is instructive to consider the ideal polarization curve for stainless steel (Figure 4.1). This curve shows how current density varies with electrochemical potential in a given corrosive medium, the current density being proportional to the corrosion rate. At low potentials (below E_p), the

alloy is in the active range and general corrosion takes place. At a
critical potential (Ecp) the current density decreases sharply and
the alloy is passivated by a thin protective surface film. The current
density at the passivation potential (Imin) is important since a low
value implies a greater ability to passivate. At very noble potentials
(above the transpassive potential, Et), the protective film breaks
down completely. There is a risk of pitting at a lower potential,
the breakdown potential, where the protective film is penetrated at
different points and where the alloy is not completely passive.

The following factors therefore increase the corrosion resistance of
a stainless steel by increasing its passivity:

(1) a stronger passivating tendency in the active zone due to
the formation of a partly protective film or insoluble
corrosion products

(2) reduction in the limiting passivation current density, Icp)

(3) minimum anodic current density value in the passive state
(Imin)

(4) more negative critical passivation potential (Ecp)

(5) more negative passivation potential (Ep)

(6) more positive potential for breakdown (Eb) of passivity
by active anions, and

(7) more positive transpassive potential (Et).

4.1.2.   Effect of Alloying Elements on the Passivity of Stainless
Steels . The influence of different alloying elements on
the characteristics of the anodic polarization curve for stainless
steel in sulphuric acid is shown in Figure 4.1. Chromium has the
most beneficial effect of all the alloying elements, but nickel,
molybdenum, silicon, copper, titanium, vanadium and others also have
a beneficial effect on the curve. The corrosion potential of an alloy
depends on the environment, so that it is possible to choose alloying
elements giving maximum corrosion resistance for a specific corrosive
environment.

It will be instructive at this stage to examine the effect of
different alloy combinations on the polarization curve. Chromium on
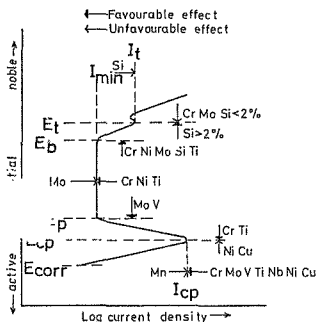
Figure 4.⬚. Effect of alloying elements on the characteristics of
the anodic polarization curve for stainless steel in
1N H_2SO_4. (Biefer, 1970; Kiesling, 1972).

Ecorr = free-corrosion potential

Ecp   = critical potential for primary passivation

Ep   = passivation potential

Eb   = breakdown (or pitting) potential

Et   = transpassive potential or secondary passivation
        potential

Icp   = critical current density for primary passivation

Imin = minimum current density for passivation

It   = transpassive current density

its own has a lower critical potential for primary passivation than
iron, so that a mixture of the two elements will produce an inter-
mediate value. A reduction in this value sufficient to benefit
corrosion resistance in neutral aqueous solutions is only achieved
at a chromium level of 12%. Increasing chromium beyond this level
will yield stainless steels which can be passivated in more aggressive
solutions, such as dilute sulphuric acid. The addition of both
chromium and nickel to the alloy will markedly facilitate passivation
since nickel further reduces the critical current density for primary
passivation, thus contracting the active (current) range of the alloy.
The result is that chromium-nickel alloys are easier to passivate
than plain iron-chromium alloys and their corrosion rate in the
active region will be lower.

Alloying an austenitic stainless steel with small amounts of molybdenum
will further reduce the critical current density and produce an alloy
that is very easily passivated, even in non-oxidizing acids.
Molybdenum-bearing, chromium-nickel stainless steels, however, have
poor propeties in the transpassive region and thus are not suitable
for highly oxidizing electrolytes such as nitric acid. Replacing
molybdenum with silicon in these steels will improve their properties
in the transpassive region.

The alloying elements discussed so far produce their effect by
shifting the anodic polarization curve in a favourable direction.
Adding a small amount of copper will not affect the anodic polariza-
tion curve significantly, but will instead facilitate the cathodic
process (reduction of the oxidizing agent) and move the free-corrosion
potential in the noble direction.

Many factors result in a break-down of the passive film with one of
the most serious as far as stainless steels are concerned being
pitting corrosion. Particular attention is therefore being given in
this study to the effects of alloying in resisting pitting corrosion.
The tendency of a metal to undergo pitting can be estimated by:

    (1) determination of the pitting potential,

(2) determination of the minimum concentration of chloride ions
    in solution causing pitting,

(3) measurement of the number and ultimately the depth and
    width of pits in a suitable standard solution, and

(4) a knowledge of the critical pitting potential of the alloy-
    ing elements present in relation to temperature.

Many factors affect the pitting corrosion of alloys, such as solution
pH and temperature, heat-treatment and cold-working, but the most
important factor from an alloy design point of view is alloying
elements. A considerable amount of work has been published on the
effects of alloying elements, and is summarized by Szklarska-Smialowska
(1971) (Table 4.1).

In the present study, while the emphasis is on the replacement of
molybdenum with vanadium, additional alloy combinations will be
examined in an attempt to improve on the properties of the molybdenum
superferritics.

4.1.3.   Nature of the Passive Film . The passive film on stainless
steels is essentially a very thin, 10 to 50Å thick, hydrous oxide.
The form of the film depends on the nature of the underlying metal,
and will therefore have different properties in areas where the
surface is inhomogeneous. Passivity is impaired over discrete
inclusions such as intermetallic compounds (e.g. chromium carbides)
and at grain-boundary precipitates. Other defects may exist where
the metal lattice is exposed to mechanical stresses or where slip
bands reach the surface.

Passivation of a metal surface requires that the entire surface be
reached by a sufficient quantity of oxidizing agent. If any part of
the surface is shielded such as in a crevice or by foreign material
on the surface, concentration gradients may arise. The concentration
of oxidizing agent may then be sufficient to passivate the free-metal
surface, but not the shielded area where the passivity will be broken
down.

Table 4.1. Effect of Alloying Elements on the Pitting Potential
            in Chloride Solutions at Room Temperature. (Iron Alloys).
            (Szklarska-Smialowska, 1971).

Element	Pitting Potential Moved to More +ve or -ve Potentials
Cr	(+)
Mo	(+), (-) at 0° C
Ni	(+) or weak positive effect
C	(-)
V, Re	(+)
Ti	(-)
Ce, Nb	(-)
Zr, Ta, W	without effect
Mn	(+) or without effect
Si	(+) or without effect

In some electrolytic solutions, generally those containing halogen
ions such as chlorides, the stability of the passive film may be
considerably reduced. Halogen ions reduce the potential range of the
passive region, particularly by lowering the breakdown potential as a
result of penetration and destruction of the passive film by the
halogen ions.

Research carried out by Frankenthal (1969) has clarified considerably
our understanding of the passivity of iron-chromium alloys. Electro-
chemical studies, accompanied by microscopic observations, on a 24%

chromium stainless steel subjected to anodic polarization in sulphuric
acid, showed that the type of film varies according to the potential
applied. There are two types of film. The primary film is stable
only within a few millivolts of the primary activation potential; its
formation or destruction is a reversible process. The thickness of
the primary film at the primary activation potential is less than the
equivalent of one atom to each surface metal atom. The secondary film
which is formed slowly at more positive potentials, grows to a thickness
greater than 10Å, and with increasing potential and sufficient time it
becomes very resistant to reduction.

In contrast to clarification on the way in which the film forms, the
picture regarding the actual composition and role of alloying elements
in the film is somewhat confused. The effect of molybdenum in improving
corrosion resistance is well known and molybdenum-containing stainless
steels have received particular attention in attempts to explain the
function of elements in the film. Several papers have been published
on the analysis of the film by Auger and X-ray photoelectron spectro-
scopy. Lumsden and Staehle (1972) examined the film on molybdenum-
containing ferritic stainless steels in sulphuric acid, sodium chloride
and sodium hydroxide and found that the improved corrosion resistance
obtained by the addition of molybdenum could not be explained by its
enrichment in the protective film. Molybdenum was not found in the
film at the potentials and pH values at which molybdenum oxide is the
stable species. The authors suggested that molybdenum may exert a
beneficial effect by improving the quality of the bonding at the metal-
oxide interface and creating a barrier layer.

In a study of a 26% chromium-molybdenum steel, Da Cunha Belo et al.
(1977) found that passivation in sodium chloride is characterized by
the formation of a thin oxide film and the development of a chromium-
depleted zone in the metallic substrate near the metal-oxide interface.
Their results are in close agreement with those of Lumsden and
Staehle (1972) and show that the molybdenum concentration in the
passive film is very low and only detectable in the inner part of the
film. It would therefore appear that molybdenum additions increase
the stability of the inner layers of the film near the oxide-metal

interface.

One of the most recent ideas on the passive oxide film (on iron) considers a semiconductor model to explain its function. Delnick and Hackerman (1979) proposed that during passivation, an electron donor is incorporated into the oxide film by the formation and migration of interstitial ions. The high electronic conductivity of the film and the unusual Tafel behaviour of passive iron is directly attributed to the presence of this donor level. According to Stimming and Schultze (1979) the passive film behaves like a highly doped, n-type semiconductor at low potentials similar to most other passive films. The most important influence of the underlying metal, they conclude, is due to stoichiometric changes at the metal-oxide interface since the metal is a constant source or sink of ferrous and ferric ions in the anodic and cathodic region. This conclusion seems to support the idea of Da Cunha Belo et al. (1977) and others that molybdenum stabilizes the film immediately next to the metal. The semiconductor approach has, however, not so far been used to explain the role of alloying elements in stabilizing the film.

To the present writer, the use of semiconductor models and the catalytic analogy (Uhlig, 1971) appear to be approaching the problem from the right direction since they consider the more fundamental aspects. It is abundantly clear that our understanding of the role of alloying elements in stabilizing the passive film depends totally on a full appreciation of the nature and function of the film; hence, present approaches can be little else but rational guesses, albeit in cases good ones.

4.2. Vanadium

Vanadium was shown by Tomashov et al. in 1964 to have a beneficial effect on the corrosion resistance, especially to pitting, of austenitic stainless steel. This fact has not been seriously followed up in subsequent publications, probably due to the overshadowing effect of molybdenum which has been known for a long time to significantly improve the corrosion resistance of stainless steels. Tomashov et al. (1964) found molybdenum to be more beneficial than vanadium

on a weight-for-weight basis, and other publications (Biefer, 1970;
Osozawa et al.,1976; Climax Molybdenum, unpublished data) have come to
the same conclusion. These publications, however, underscore the fact
that vanadium is beneficial and it is the purpose of this study to
explore in full the degree to which vanadium can replace molybdenum
while still maintaining, or improving on, good corrosion resistance.

Moody (1979) and McQueen (1979) have carried out literature surveys to
examine the effect of vanadium and other alloying elements on the
corrosion resistance of stainless steels. Moody concludes that
vanadium has a beneficial effect on the pitting resistance although not
to the extent as shown by molybdenum or rhenium. McQueen considers
that the molybdenum in stainless steels can be partially replaced with
silicon or vanadium.

A thorough literature survey by the present author has revealed some
13 publications and other sources which have examined the effect of
vanadium on the corrosion resistance of stainless steels. A summary
of the conclusions from these papers is presented in Table 4.2.

An anomalous situation with regard to vanadium is that the pure metal
can, according to the Pourbaix diagram (Figure 4.2.), dissolve in acids
and alkalies. In practise, however, vanadium is resistant to attack
by HCl and dilute H_2SO_4 and to alkaline solutions and improves the
passivity when alloyed in stainless steels. Clearly, vanadium is able
to passivate more extensively in various media than is predicted by
the Pourbaix diagram.

Table 4.2. Effect of Vanadium on the Corrosion Resistant Properties
of Stainless Steels : Summary from Literature Survey

Type of Corrosion, with Reference	Alloy	Effect of Vanadium
1. Pitting Corrosion		
a) Tomashov et al. (1964)	18Cr-14Ni 0-4.75%V	Improves pitting resistance by increasing the pitting potential. Corrosion rate negligible at 4.75% V in $FeCl_3$.

Type of Corrosion with Reference	Alloy	Effect of Vanadium
b) Biefer (1970)	17Cr	Reduced corrosion rate in H_2SO_4, HCl and $FeCl_3$. Increased rate in HNO_3. Beneficial effect on critical anodic polarization curve.
c) Osozawa et al. (1976)	17Cr-16Ni 0-3.3%V	Corrosion rate in $FeCl_3$ reduced by 40%. Alloying V with Mo increases corrosion rate.
d) Climax Molybdenum (unpublished data)	18Cr 0-3%V	Increased pitting potential. Reduced corrosion rate in chloride solution, and formic acid. Negligible corrosion in 0.1N HCl (O_2 saturated).
e) Agarwala and Biefer (1972)	17Cr 1.8%V	Improves corrosion resistance in H_2SO_4 +NaCl when alloyed with Pd, but not with Ge or Re. In HCl and $FeCl_3$ corrosion increased when alloyed with Pd, Ge or Re. Beneficial and detrimental effects on anodic polarization curve.
f) Truman (Data from Moody, 1979)	18Cr-15Ni 0-1.8%V	Beneficial effect on passivation potential in H_2SO_4, and pitting potential in NaCl.
g) Truman (1953)	18Cr-4Ni 0 and 4%V	No pitting at 4%V in chloride solution. Improves passivation in H_2SO_4.
	18Cr-12-14%Ni 0-5%V	Pitting potential decreases slightly with increasing V.
h) Floreen (1980)	24Ni-9Cr 2%V	Slight beneficial and detrimental effects when alloyed with Cu and Si.

Type of Corrosion, with Reference	Alloy	Effect of Vanadium
i) Aslund (1977)	18Cr–2Mo 1.1%V	Detrimental effect when combined synergistically with Ti to raise pitting potential.

2. **Intergranular Corrosion**

a) Lula et al.(1954)	18Cr 0.14–1.3%	No effect.
b) Houdremont and Tofaute (1952)	18Cr–8Ni 2.02%V	No effect.
c) Odesskii et al. (1978)	18Cr 1–1.5%	Resistant to intergranular corrosion (carbon level 0.08%).

3. **Oxidation Resistance**

a) Truman and Pirt (1976)	11–12Cr 0.1–0.2%V	Relatively little effect.
b) Truman and Pirt (1976)	18Cr–15Ni 0.9–1.8%V	Adverse effect below, but beneficial effect above, 750°C

4. **General Corrosion**

a) Moody (1979)	11–12Cr–11Ni 1–6%V (plus Cu, Mo, Co)	Beneficial effect on corrosion rate in HCl and H_2SO_4.
b) Odesskii et al. (1978)	18Cr–1.5%V	Resistance to food acids equals that of Type 304.
c) Floreen (1980)	24Ni–9Cr 2%V	Improves passivation character- istics and reduces corrosion rate in H_2SO_4.

5. **Stress-Corrosion Cracking**

a) Truman (Data from Moody, 1979)	18Cr–15Ni 0–1.8%V	No failure in high-carbon alloys (0.11% carbon). However, reduces failure time when carbon level lowered (0.045%).

Type of Corrosion with Reference	Alloy	Effect of Vanadium
b) Odesskii et al. (1978)	18Cr 1-1.5%V	Resistant to cracking.
c) Floreen (1980)	24Ni-9Cr 2%V	Reduces time to cracking.

6. Atmospheric Corrosion

a) Truman (Data from Moody, 1979)	18Cr-15Ni 0-1.8%V	Variable results on exposure to atmosphere for 18 months.
b) Odesskii et al. (1978)	18Cr 1-1.5%V	No trace of corrosion observed in salt spray tests or in tropical climate.
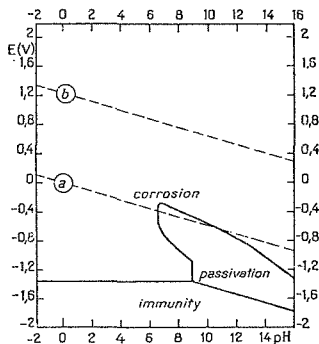
Figure 4.2. Pourbaix diagram for the system V-H$_2$O at 25°C.(Pourbaix, 1966). The dashed lines delineate the zone of stability of water and represent equilibria between water and oxygen (b) and water and hydrogen (a).

4.2.1. Pitting Corrosion. The most comprehensive publications examined all deal with the effect of vanadium on pitting corrosion. Clearly, this is the field of corrosion where its most beneficial effects have been noted to date.

Tomashov et al. (1964) studied the effect of vanadium and other elements on the pitting corrosion resistance of an 18Cr-14Ni stainless steel containing 360 ppm carbon and prepared by solution annealing at 1150°C and water quenching. The corrosion rate of the alloy in 0.5N $FeCl_3$ was found to increase when 2% vanadium was added, but decreased thereafter until at 4.75% corrosion was negligible (Figure 4.3; note also the beneficial effect of silicon and molybdenum, and the detrimental effect of titanium and niobium).

Vanadium increased the pitting potential in 0.1N NaCl with the result that no breakdown was observed up to a potential of 1.5 volts (relative to the hydrogen electrode) for a vanadium concentration of 5%.

In 0.1N HCl, alloying with 5% vanadium improved the pitting potential of the base alloy by 100 mV (as did 5% silicon). Of the alloying elements examined, molybdenum produced the best effect by raising the pitting potential of the base alloy by 800 mV (for a 5% concentration).

Biefer (1970) examined the effect of vanadium and other elements on the corrosion resistance of Type 430 stainless steel using polarization and corrosion rate measurements. In the concentration range 0 to 2.18%, vanadium was found to significantly reduce the corrosion rate in 1N H_2SO_4 and 1N HCl (Figure 4.5), to reduce the rate only slightly in $FeCl_3$, and to cause an increase of about 100% in the rate in boiling 65% HNO_3. It may be noted that an increase in the molybdenum concentration from 1.48 to 3.11% in the base alloy resulted in a more than 200-fold increase in the corrosion rate in boiling 65% HNO_3, due to intergranular corrosion
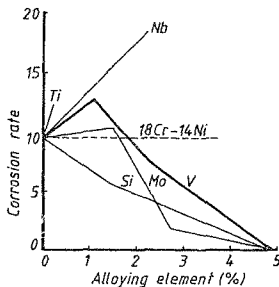
Figure 4.3. Effect of vanadium and other alloying elements on the corrosion rate of an 18Cr-14Ni alloy in 0.5N FeCl₃. Duration of test was 68 hours, at room temperature. Potentials relative to normal hydrogen electrode. (Tomashov et al., 1964).
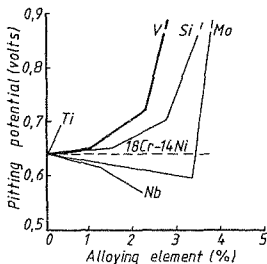
Figure 4.4. Effect of vanadium and other alloying elements on the pitting potential of an 18Cr-14Ni alloy in 0.1N NaCl. Temperature 25°C. Potentials relative to normal hydrogen electrode. (Tomashov et al., 1964).
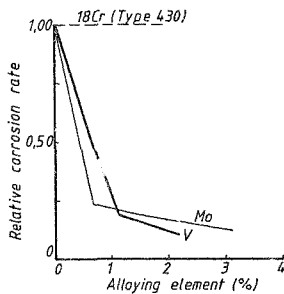
Figure 4.5. Effect of vanadium and other alloying elements in decreasing the corrosion rate of Type 430 stainless steel in 1N HCl and 1N H_2SO_4. (Biefer, 1970).

Anodic polarization measurements in 1N H_2SO_4 and 0.5N NaCl showed that
vanadium had a beneficial effect on the potential and current density
for primary passivation as well as on other points. The pitting
potential decreased somewhat in nitrogenated 1N H_2SO_4 as vanadium
increased from 0 to 1.3%, but rose abruptly at a concentration of 2.18%
(+316 to +488 volts; relative to the saturated calomel electrode).
Biefer (1970) did not remark on this significant trend, one which is
also shown by the $FeCl_3$ results of Tomashov et al. (1964).

The most important data as far as the present study is concerned is
unpublished work from the Climax Molybdenum (U.S.A.). Vanadium, in
concentrations of 1, 2 and 3%, was added to 18 and 24% chromium
superferritic stainless steels containing a combined carbon and
nitrogen level of 300 ppm. The results of polarization and corrosion
rate measurements for vanadium are shown in Table 4.3, as well as
those for molybdenum in Table 4.4 for direct comparison.

Vanadium additions to both the 18 and 24% chromium steels are seen to
improve the pitting resistance of the alloy in various chloride—
containing solutions, although not as much as found for molybdenum on
a weight-for-weight basis. A significant result from Table 4.3 is
the ability of 3% vanadium to confer resistance to intergranular
corrosion in the Fe-Cr-V alloy. This result has important consequences
regarding the level of vanadium needed as a stabilizer in ferritic
stainless steels.

In the work of Osozawa et al. (1976), 2% vanadium was found to reduce
the corrosion rate of a 17Cr-16Ni alloy in $FeCl_3$ by about 35%.
Increasing the vanadium level to 3.3% had very little effect on the
corrosion rate. The pitting potential increased slightly over the
same concentration range in an acidified chloride solution. In marked
contrast, adding molybdenum and vanadium together produced an
increase in the corrosion rate in $FeCl_3$. (The same effect was noted
when combining molybdenum with titanium, niobium or copper).

Agarwala and Biefer (1972) carried out ...   ...ermine whether
elements affecting anodic polarizatio   vanadium, molybdenum
and tungsten) could be combined synergis: ith elements primarily

Table 4.3. Corrosion Properties of Vanadium-Bearing Superferritic Stainless Steels (Unpublished data from Climax Molybdenum)

Nominal Composition [a]	Heat Treatment	Pitting Potential in 1N NaCl (volts)		Corrosion Rate (mdd)					Intergranular Corrosion Tests	
		25°C	45°C	10% FeCl₃ + .1N HCl 25°C	600ppm Cl⁻ 5ppm Cu⁺⁺ O₂ Sat'd 90°C	0.1N HCl O₂ Sat'd 25°C	10% Formic Acid (Boiling)	45% Formic Acid (Boiling)	Streicher	Strauss
18Cr	816°C 1 Hr WQ			554			114,000			
18Cr -1V	816°C 1 Hr WQ	.28			14.4	0.0	7,210		345	Failed[b]
-2V	816°C 1 Hr WQ	.33			2.9	0.0	7,020		405	Failed[b]
-3V	816°C 1 Hr WQ	.36		2,200	1.9	0.0	5,800		454	Passed[b]
3V.45Ti	816°C 1 Hr WQ			2,900	4.0	0.0			512	Passed[b]
22.5Cr	816°C 1 Hr WQ		.27		0.0	0.0	0.0	32,700		
24Cr -1V	816°C 1 Hr WQ		.34	114	0.0	0.0	0.0	4,410	119	Failed[t]
-2V	816°C 1 Hr WQ		.52	55.6	1.0	0.0	0.0	4,010	125	Failed[b]
-3V	816°C 1 Hr WQ		.52	568	0.0	0.0	0.0	3.9	120	Passed[b] Passed[c]
3V.40Ti	816°C 1 Hr WQ		.64	471	0.0	0.0	0.0	4.3	123	Passed[c] Passed

(a) C + N = 300 ppm   (b) 1149°C, 15 min. WQ   (c) 1200°C, 5 min. AC

Table 4.4. Corrosion Properties of Molybdenum-Bearing Superferritic Stainless Steels (Unpublished data from Climax Molybdenum)

Nominal Composition	Heat Treatment	Pitting Potential in 1N NaCl (volts)		Corrosion Rate (mdd)					Intergranular Corrosion Tests	
		25°C	45°C	10% FeCl₃ + .1N HCl 25°C	600ppm Cl⁻ 5ppm Cu⁺⁺ O₂ Sat'd 90°C	10% Formic Acid (Boiling)	45% Formic Acid (Boiling)		Streicher	Strauss
18Cr-2Mo -.008C-.019N	916° C 1 Hr WQ	---	---	600	1.0		57,000			Failed[a] Failed[b]
18Cr-1.8Mo -.020C-.007N -.23Ti	816° C 1 Hr WQ	.8	.58	2900	nil	nil	1,100			Passed[a] Passed[b]
19Cr-1.8Mo -.015C-.010N -.11Ti	916° C 1 Hr WQ	.8	.67	2600						Failed[a] Failed[b]
18Cr-2Mo -.03C-.045N -.47Ti	816° C 1 Hr WQ	.7	.30	1250		15				Passed[a] Passed[b]
18Cr-C-Mo -.03C-.03N	1 Hr	.07	-.03	7200		75,000			153	
18Cr- -.03C-	...C 1 Hr	.18	.04	7700		64			125	
18Cr- -.03C-.03N	...C 1 Hr WQ	.25	.10	5300		40			90	Failed[c]
18Cr-3.5Mo -.03C-.03N	816° C 1 Hr WQ	.3	.13	670		38			144	
26Cr-1Mo -.012C-.010N	788° C 2 Hr WQ		.62	0.0					3511[b]	Failed[d]

Table 4.4. Corrosion Properties of Molybdenum-Bearing Superferritic Stainless Steels (continued)

Nominal Composition	Heat Treatment	Pitting Potential in 1N NaCl (volts)		10% FeCl$_3$ + .1N HCl	Corrosion Rate (mdd)			Intergranular Corrosion Tests	
		25°C	45°C	25°C	600ppm Cl$^-$ 5ppm Cu^{++} O$_2$ Sat'd 90°C	10% Formic Acid (Boiling)	45% Formic Acid (Boiling)	Streicher	Strauss
26Cr-2Mo -.01C-.005N	788°C 2 Hr WQ		1.0	0.0				625[b]	Failed[a]
24Cr-2.8Mo -.01C-.021N -.29Ti	927°C 1 Hr WQ		1.0	0.0					Passed[a] Failed[b]

(a) 1149°C 15 Min. WQ   (b) TIG welded   (c) 927°C 1 Hr WQ   (d) 1204°C 5 Min. AC

affecting cathodic polarization behaviour (palladium, germanium and rhenium) to produce Type 430 steels having improved corrosion behaviour. Only the palladium-bearing steels showed some promise. Steels containing 2% vanadium + 1% palladium (also 2% molybdenum + 1% palladium) readily passivated in 1N H_2SO_4 containing 0.5N NaCl, whereas in previous work Biefer (1970) had shown that vanadium alone did not produce passivation. Vanadium in combination with germanium or rhenium did not show good corrosion resistance, failing to passivate in 1N H_2SO_4.

In a study on the use of vanadium as a stabilizer in a 18Cr-2.4Mo (Type 444) stainless steel, Walarui (1977) found that the addition of 0.1% vanadium reduced the pitting potential in 0.5M NaCl (from 525 mV for the 18Cr-2.4Mo-0.35Ti alloy to 110 mV). Combining 0.1% vanadium with 0.35% titanium, however, had a synergistic effect in raising the pitting potential to 650 mV.

Unpublished data by Truman (1953) shows that vanadium had a variable effect on the pitting potential in a chloride medium, depending on the chromium level (Table 4.5). The pitting potential decreased in the 17 and 18% chromium alloys, but increased significantly when chromium was increased to 25%. This decrease in potential at between 2.3 and 5% vanadium is somewhat at variance with the results presented above, possibly due to differing interstitial levels. Weight loss experiments in 1N H_2SO_4 showed somewhat variable results.

4.4.2.   Intergranular Corrosion. Lula et al. (1954) examined the effect of various elements on the intergranular corrosion of 18% chromium ferritic stainless steels containing 320 - 580 ppm carbon. As-welded samples from alloys containing 0.14% vanadium (titanium stabilized) and 1.3% vanadium (unstabilized) showed severe lines of attack adjacent to the weld and some intergranular attack of the weld deposit in both acidified $CuSO_4$ and boiling 65% HNO_3. It was concluded that vanadium did not remove susceptibility to sensitization. Houdremont and Tofaute (1952) came to the same conclusion in connection with an 18Cr-8Ni steel alloyed with 2.02% vanadium.

Table 4.5.   The Effect of Vanadium and Molybdenum on the Pitting
             Potential of Austenitic Stainless Steels in 0.6N
             NaCl + 0.1N NaHCO$_3$.   (Truman, 1953).

Alloy Composition					Pitting Potential
Cr	Ni	Ti	V	Mo	(mV, SCE)
17	13.5	–	–	–	+374
17	13.5	–	1.0	–	+368
17	13.5	–	5.0	–	+322
25	4.1	0.4	–	–	+320
25	4.0	0.4	4.0	–	+1026	No pitting –
25	4.0	0.4	–	3.9	+1004	transpassive region.
18	–	0.4	–	–	+192
18	–	0.4	1.3	–	+112
18	–	0.4	–	2.3	+356

Note: Carbon content not specified but probably in the range 0.06-0.1%

According to Aslund (1977), vanadium shows promise as a stabilizing
element but does not inhibit intergranular corrosion. Odesskii et
al. (1978) reported that an 18Cr-1 to 1.5V alloy with 0.08% carbon is
resistant to intergranular corrosion.

4.2.3.   Oxidation Resistance.   The effect of various alloying elements
on the resistance to oxidation at elevated temperatures of an 18Cr-15Ni
austenitic stainless steel was considered by Truman and Pirt (1978).

Vanadium additions up to 0.91% appeared to have an adverse effect
on oxidation resistance at some temperature below 750°C and a
beneficial effect above this value.

In a similar study carried out by the same authors on 10-12Cr-0.2V
alloys (Truman and Pirt, 1976), vanadium had relatively little
effect on oxidation resistance, as was also the case for
molybdenum.

4.2.4.   General Corrosion . In unpublished work (Moody, 1979)
carried out by Edenleanu (Brown-Firth Research Laboratories) on
the development of a stainless steel resistant to HCl, vanadium
was added to an 11 to 12Cr-11Ni alloy in amounts from 1 to 6%,
alone and in combination with copper and molybdenum. Weight loss
measurements on the alloys in HCl and H_2SO showed that 6%
vanadium increased the corrosion rate up to 7 times compared
to the base alloy.

In the work of Odesskii et al.,(1978), an 18Cr-1-1.5%V alloy
was found to have the same resistance to food acids as Type 304
stainless steel.

4.2.5.   Stress-Corrosion Cracking . Vanadium, in concentrations
from 0.9 to 1.8%,has been found to confer immunity to stress-
corrosion cracking (testing to 500 hours) on an 18Cr-15Ni
austenitic alloy in boiling $MgCl_2$ when combined with a relatively
high carbon content (0.11%)(Moody, 1979). When the carbon
content was lowered to 400-500 ppm the time to cracking
decreased in comparison to the vanadium-free steel (Table 4.6).
This fact has important consequences for austenitic stainless
steels which normally undergo stress-corrosion cracking in
$MgCl_2$.

Table 4.6.   The Effect of Vanadium on Stress-Corrosion Cracking
             in 18Cr-15Ni Stainless Steel. (Moody, 1979).

Vanadium (Carbon) Level	Time to Rupture (Hours)	
	Boiling 42% MgCl$_2$	3% NaCl at 250°C and 103 MPa
0.91%V (0.04%C)	63	
1.79%V (0.05%C)	150	
0.91%V (0.11%C)	500 ⎱ No cracks	500 ⎱ No cracks found
1.67%V (0.11%C)	500 ⎰ found	500 ⎰

4.3.   Molybdenum

The principal functions of molybdenum as an alloying element in
stainless steels are: improvement of corrosion resistance, improvement
of elevated temperature properties of austenitic stainless steels, and
improvement of the strength and resistance to tempering of martensitic
stainless steels. Molybdenum is well known for the beneficial effect
it has on corrosion resistance, being present in ferritic Types 434 and
436 (1%), austenitic Type 316 (2%) and the superferritic stainless
steels. Its main purpose is to resist pitting corrosion but it is also
beneficial in sea-water, dilute reducing acids and organic acid
environments.

Although the object of the present study is to replace molybdenum
totally, it may be possible to obtain a better result by combining
some molybdenum with vanadium, so that the effects of the element
should be appreciated.

4.3.1.   Pitting and Crevice Corrosion. The metal molybdenum is very
resistant to pitting in various aqueous media and this fact is
reflected in the effect it has as an alloying element in stainless
steels.

The effect of molybdenum in increasing the pitting potential and
hence resistance to pitting corrosion of an 18% chromium stainless

steel is shown in Tables 4.7 and 4.4 .   Lizlovs and Bond (1971)
also found that molybdenum improved the resistance to crevice
corrosion in chloride media although it did not confer immunity
to this form of corrosion.

Correct heat-treatment and stabilization are necessary in
stainless steels containing more than 2% molybdenum in order
to avoid the formation of chi phase and a consequent reduction
in corrosion resistance.   Bond (1973)found that annealing at
815°C and water-quenching led to the formation of chi phase
in 18Cr-Mo alloys. In an attempt to remove the chi-phase,
annealing was carried out at 980°C but this lowered the
pitting potential considerably in 1N NaCl.   Stabilization,
resulting in the immobilization of carbon and nitrogen, was found
to be the only means of reducing the precipitation of the
chi-phase.

The effect of molybdenum is dependent to ε   nt on the
amount of chromium present.   Lizlovs and   /75)
found that complete passivity did not occur in   a chromium
steel in 1N HCl, even with the addition of 5% molybdenum.
Increasing the chromium content to 18%, however, resulted in
complete passivation thus showing that molybdenum and chromium
are acting synergistically.   In the same study it was found
that the pitting potential increased linearly with molybdenum
content, and more rapidly for the 18 than 13% chromium
steels.   All alloys underwent pitting corrosion in 10% FeCl$_2$
(up to 5% molybdenum) although those with a higher chromium-
molybdenum content pitted the least and showed the smallest
weight losses.   Interestingly, the addition of 1% molybdenum
to both 13 and 18% chromium alloys increased rather than
decreased the corrosion in FeCl$_3$ relative to the molybdenum-
free alloy.

Table 4.7.   Average Pitting Potentials of Some Ferritic Stainless
             Steels in 0.1 N HCl. (Lizlovs and Bond, 1969).

Steel	Average Pitting Potential vs. SCE (Volts)
Type 430	0.18
Type 434	0.19
17Cr	0.26
17Cr-1Mo	⌐.32
17Cr-3Mo	> 0.80
18Cr-2Mo-0.11Ni	0.31
18Cr-2Mo-0.62Ni	0.35
18Cr-2Mo-1.08Ni	0.34
18Cr-2Mo-0.47Ti	> 0.80
18Cr-2Mo-1.86Ti	0.63
18Cr-2Mo-0.91Ti-0.57Ni	> 0.80
18Cr-2Mo-1.75Ti-2.08Ni	0.62

Note. Test temperature was 30°C, except for 18Cr-2Mo alloys
      where it was 24°C.

4.3.2.   Stress-Corrosion Cracking .   The behaviour of molybdenum is
ill-defined but on balance it appears to have a detrimental effect on
stress-corrosion cracking in stainless steels. It is definitely
deleterious at the lower concentration range in boiling $MgCl_2$
solutions, promoting intergranular stress-corrosion cracking in
austenitic stainless steels (Hanninen, 1979).

The addition of small amounts of molybdenum to Fe-Cr stainless steels
(e.g. 18Cr-2Mo) does not produce susceptibility to stress-corrosion
cracking. In larger amounts (in excess of 4 to 6%) depending on the
chromium level, molybdenum leads to cracking in Fe-Cr stainless steels
exposed to boiling $MgCl_2$ (Streicher, 1974). When present together
with nickel, however, molybdenum proves to be detrimental in Fe-Cr
ferritic stainless steel. Bond and Dundas (1968) found that whereas
a 17Cr-1.5Ni alloy did not crack in $MgCl_2$, an 18Cr-0.5Ni-1Mo alloy
did. It has been suggested that failure in Cr-Ni-Mo steels is due to

the formation of intermetallic Ni_3Mo, analogous to the formation of
Ni_3Ti in maraging steel. (Thompson and Bernstein, 1979).

Desestret and Wagner (1969) studied the effects of molybdenum (and
silicon) on the stress-corrosion cracking of duplex stainless steels
in boiling $MgCl_2$, $CaCl_2$, NaCl, water (150 and 200°C) and hot steam
at 500°C. Molybdenum caused cracking in boiling $MgCl_2$, but not in the
other media.

Table 4.8.   Corrosion Rates for Stainless Steels in Boiling Acids
              and Alkali showing the Effect of Adding Molybdenum.
              (Streicher, 1977).

	Corrosion Rate (mm per year)			
	Type 304	Type 316	Type 430	Type 444
65% HNO_3	0.2	0.3	0.5	5.8
50% H_2SO_4 + $Fe_2(SO_4)_3$	0.6	0.6	7.9	4.1
45% Formic Acid	44	13	2200	10
10% Oxalic Acid	15	2.4	160	250
20% Acetic Acid	0.1	0.1	80	0
10% Sodium Bisulfate	70	4.3	2300	930
10% H_2SO_4	400	22	6400	2400
1% HCl	81	71	1500	850
60% NaOH (100°C)	118	106	–	945

4.3.3.   General Corrosion.   A comparison of the corrosion rates for
Types 304 and 316 alloys in various media (Table 4.8) shows that
molybdenum has a beneficial effect on corrosion resistance.
Molybdenum at the 2.5% level is found to reduce hydrogen evolution in
most of the reducing acids but has little effect on corrosion in the
two oxidizing solutions. Molybdenum acts in a similar way to nickel
in combining with chromium to improve the corrosion resistance in
reducing acids. Figure 4.6. shows that small additions of molybdenum
(1 to 2%) have the greatest effect in reducing the critical current
density for primary passivation in H_2SO_4.
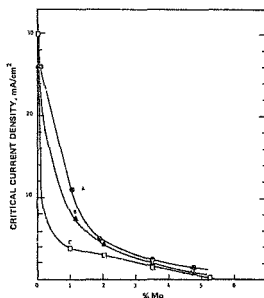
Figure 4.6.   The effect of molybdenum (and chromium) on the ease of
              passivation of low-interstitial ferritic stainless
              steels in 1N H_2SO_4 (30°C). A - 13Cr; B - 18Cr;
              C - 25Cr. (Steigerwald et al., 1977).

The ease of passivation in chromium-molybdenum ferritic alloys is
promoted not only by a reduction in the critical current density but
also by a shift in the primary passivation potential to more active
values (Greene, 1962). In addition to reducing the critical current
for iron, both chromium and molybdenum shift the primary passivation
potential to more active values. The reduced critical current density
and active passivation potential account for the good resistance of
the Fe-Cr-Mo combination to organic acids.

4.4   Nickel

Ferritic stainless steels do not normally contain nickel as a
deliberate alloying element because it can increase susceptibility to
stress-corrosion cracking. In the more recently developed low-inter-
stitial high-chromium ferritic alloys, however, nickel is added to

improve corrosion resistance to sea water and in other aggressive
environments such as found in the pulp and paper industry (e.g. the
Swedish Nyby AB Monit alloy - 25Cr-4Mo-4Ni.)

Two of the main drawbacks to the use of ferritic stainless steels are
poor impact strength and corrosion resistance, especially in inorganic
reducing acids. Nickel has a beneficial effect on both these
properties and should therefore be considered as an alloying addition
to obtain improved types of ferritic stainless steels. The only
problem is the susceptibility of low nickel-bearing ferritic stainless
steels to stress-corrosion cracking in $MgCl_2$, especially in the presence
of molybdenum. This is a further motivating point for examining the
effect of vanadium-nickel combinations in stainless steels.

4.4.1.   General Corrosion . Nickel has a beneficial effect on the
corrosion resistance of stainless steels in most environments as can
be seen by comparing the results for Types 304 and 430 alloys in
Table 4.8. Of particular interest in the present study are small
additions of nickel (up to 2-3%) because of the possibility of stress-
corrosion cracking at a higher level. As was the case for molybdenum,
the first few percent of nickel has the greatest effect in lowering
corrosion in reducing acids (Figure 4.7). The beneficial effect of
nickel on passivation characteristics in ferritic stainless steels
has been noted in the literature (Chernova and Tomashov, 1965;
Binder, 1965; Lizlovs and Bond, 1971). Lizlovs and Bond found that
an increase in nickel from 1 to 2.5% decreased the critical current
density of a 25Cr-3.5Mo alloy in 1N H_2SO_4, to the extent that critical
behaviour was suppressed completely. The same authors (1969) noted
a synergistic effect between nickel and molybdenum in ferritic stain-
less steels in that an 18Cr-Ni alloy did not completely passivate in
1N HCl, except in the presence of molybdenum.

A particular drawback of the 18Cr-2Mo alloy is that it possesses a
high corrosion rate in the active state, and it depends on passivity
for resistance to acids. As a result it shows sharp transitions from
active to passive behaviour depending on the acid concentration and
temperature. Austenitic stainless steels have low corrosion rates in

improve corrosion resistance to sea water and in other aggressive
environments such as and in the pulp and paper industry (e.g. the
Swedish Nyby AB Monit . ov - 25Cr-4Mo-4Ni.)

Two of the main drawbacks in the use of ferritic stainless steels are
poor impact strength and corrosion resistance, especially in inorganic
reducing acids. Nickel has a beneficial effect on both these
properties and should therefore be considered as an alloying addition
to obtain improved types of ferritic stainless steels. The only
problem is the susceptibility of low nickel-bearing ferritic stainless
steels to stress-corrosion cracking in $MgCl_2$, especially in the presence
of molybdenum. This is a further motivating point for examining the
effect of vanadium-nickel combinations in stainless steels.

4.4.1. General Corrosion . Nickel has a beneficial effect on the
corrosion resistance of stainless steels in most environments as can
be seen by comparing the results for Types 304 and 430 alloys in
Table 4.8. Of particular interest in the present study are small
additions of nickel (up to 2-3%) because of the possibility of stress-
corrosion cracking at a higher level. As was the case for molybdenum,
the first few percent of nickel has the greatest effect in lowering
corrosion in reducing acids (Figure 4.7). The beneficial effect of
nickel on passivation characteristics in ferritic stainless steels
has been noted in the literature (Chernova and Tomashov, 1965;
Binder, 1965; Lizlovs and Bond, 1971). Lizlovs and Bond found that
an increase in nickel from 1 to 2.5% decreased the critical current
density of a 25Cr-3.5Mo alloy in 1N H_2SO_4 to the extent that critical
behaviour was suppressed completely. The same authors (1969) noted
a synergistic effect between nickel and molybdenum in ferritic stain-
less steels in that an 18Cr-Ni alloy did not completely passivate in
1N HCl, except in the presence of molybdenum.

A particular drawback of the 18Cr-2Ni alloy is that it possesses a
high corrosion rate in the active state, and it depends on passivity
for resistance to acids. As a result it shows sharp transitions from
active to passive behaviour depending on the acid concentration and
temperature. Austenitic stainless steels have low corrosion rates in

the active state due to the presence of nickel and they therefore show
substantially improved corrosion resistance in inorganic acids such
as H_2SO_4.

Nickel does not appear to have any effect on the intergranular corrosion
resistance of ferritic stainless steels in the range 2 to 5% nickel
(Baerlocker et al., 1961). When nickel promoted austenite formation,
however, resistance to intergranular corrosion was found to be
greatly improved.

% Ni	Steel
0.3	AISI 430
0.5	18Cr-15.5Mn-0.5Ni
1.0	15Cr-17Mn-1.0Ni
4.4	17.6Cr-5.6Mn-4.4Ni
10.5	AISI 304
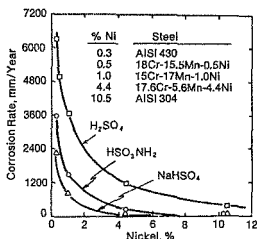
Figure 4.7.   The influence of nickel on the corrosion of stainless
              steels in boiling acids (10%). Active state.
              (Streicher, 1977).

4.4.2.   Stress-Corrosion Cracking.   The role of nickel in the stress-
corrosion cracking of ferritic stainless steels is complex, and depends
in addition to the nickel level, on the presence of other alloying
elements, cold-working, interstitial level and micro-structure. The
Copson curve relating the nickel content to the time of cracking of
stainless steels in $MgCl_2$ is widely referred to (Copson, 1959).

Poulson and Parkins (1973), have shown that the addition of nickel to
a conventional ferritic stainless steel containing 0.06-0.1% carbon

caused stress-corrosion cracking in boiling $MgCl_2$. The time to
failure decreased up to 2% nickel, then increased gradually to 6%
(the maximum nickel content studied). On the other hand, Bond and
Dundas (1968) showed that vacuum- and air-melted 18% chromium ferritic
alloys with carbon levels of 40 and 350 ppm respectively and contain-
ing up to 1.5% nickel did not cra⸱ ᶟ the same solution (Table 4.9).
The authors found that cracking onl⸱ ̤ccurred when about 1% or more
nickel was present together with mo'ybdenum in the alloy. In tests
less severe than boiling $MgCl_2$, for example the sodium chloride wick
test which is often considered to be more representative of the work
situation, the combination of nickel and molybdenum does not lead to
cracking.

Cold-working is another factor enhancing the stress-corrosion effect
of nickel in ferritic stainless steels. Bond and Dundas (1968)
found that a 17% chromium alloy containing 1.5% nickel became
susceptible to cracking when cold-worked, but was resistant when
correctly annealed (Table 4.9).   Interstitial element level is
found to affect cracking susceptibility, more particularly in high-
purity alloys. Snape (1977) reports that an electron-beam melted
26Cr 1Mo-2.6Ni alloy did not crack in boiling $MgCl_2$. No apparent
relationship between interstitial element content and nickel is
evident in the results of Bond and Dundas (1968) for ferritic alloys
containing from 20 to 690 ppm carbon.

Microstructure appears to have an important influence on the stress-
corrosion cracking of stainless steels. Wylie (1962) patented a
martensitic-ferritic stainless steel containing both nickel and
molybdenum which did not undergo cracking in various chloride media
(Table 4.10). The alloy showed good impact strength at low
temperatures, good weldability and excellent mechanical properties at
moderately elevated temperatures. A similar duplex-type alloy has
been described by Truman (1968) which showed good stress-corrosion
cracking resistance. In contrast to these results, Matsushimia and
Ishihara (1975) report that the formation of other phases, such as
martensite and austenite, due to the nickel addition increased the
susceptibility to stress-corrosion cracking of an 18% chromium alloy
with up to 1.5% nickel.

Table 4.9. Stress-Corrosion Cracking of U-bend Specimens of Ferritic Stainless Steels in Boiling (140°C) MgCl₂. (Bond and Dundas, 1968).

Alloy (%)	Time to Failure (hr)
Air Cast Alloys (a)	
18Cr-1Ni	146 NF
18Cr-1Ni-1Mo	4-22
18Cr-1Ni-5Mo	4-43
Vacuum-Melted Alloys (b)	
18Cr-0.6Ni	620 NF
18Cr-1.5Ni	722 NF
18Cr-1.5Ni (cold-rolled)	28-92
25Cr-3.5Mo	475 NF
25Cr-1Ni-3.5Mo	22
25Cr-4Ni-3.5Mo	5.5

(a) 350 ppm carbon   NF - no failure

(b)   40 ppm carbon

Table 4.10 Stress-Corrosion Cracking Resistance of Smooth Tension Specimens of 15.7Cr-2.5Ni-1Mo-0.5Nb-0.03C-0.5Si-0.6Mn Stainless Steel Exposed to Various Chloride Solutions. (Wylie, 1962).

Chloride Solution	Time to Failure (hr)
42% boiling MgCl₂	500 NF
3% NaCl at 250°C	500 NF
Specimen coated with NaCl and held at 330°C in steam	3250 NF
Specimen from simulated crevice in heat-transfer surface. (Water contained 1000 ppm NaCl and metal temperature was 330°C)	

NF - no failure

4.4.3. _Pitting Corrosion_ . Nickel does not have a strong effect on the pitting resistance of ferritic stainless steels, but on balance it appears to be beneficial (compare the 18Cr-2Mo alloys in Table 4.7). Nickel is reported to increase the pitting resistance of a 21% chromium alloy in 0.5N FeCl$_3$ and potentiostatic polarization measurements show that nickel increases the potential at which the passive film undergoes breakdown in 3% NaCl(Langer et al., 1966).

The high-chromium superferritic stainless steels (e.g. 28Cr-4Ni-2Mo) contain nickel in order to improve general corrosion resistance and toughness for very aggressive environments, although it does reduce the stress-corrosion cracking resistance of the alloys.

4.5. _Silicon_ . Silicon is present as a residual element in all stainless steels, including superferritics, to the extent of about 0.5%. The chief advantage of deliberately alloying ferritic stainless steels with silicon is in resistance to scaling and oxidation at elevated temperatures, with levels as low as 1% raising the temperature at which free scaling commences. With respect to corrosion resistance, silicon alone has little effect unless in amounts greater than 1%, at which level there is increased resistance to cold acids, such as nitric, sulphuric, citric and oxalic. Resistance to hydrochloric, acetic or concentrated hot nitric acids does not appear to be improved. Silicon cannot be added to stainless steels in amounts exceeding about 3% because of it increases the susceptibility to sigma phase formation.

4.5.1. _Pitting Corrosion_ . The effect of silicon on the pitting resistance (and passivation) of stainless steels has been mentioned briefly in previous sections.

Silicon appears to have been one of the first elements considered in early attempts to improve the pitting resistance of austenitic and ferritic stainless steels. Streicher (1956) reported the development of an austenitic Type 316L alloy containing 2.5% silicon and 0.23% nitrogen. This alloy (code named SP-2) was found to be resistant to aggressive pitting solutions such as KMnO$_4$/NaCl up to 50°C (Table 4.11). The removal of nickel from the alloy in order to improve resistance to stress-corrosion cracking lead to fabrication problems although the

resulting alloy was still as resistant to pitting in $KMnO_4$/NaCl as the SP-2 alloy. Because of these problems molybdenum was used in place of silicon in ferritic type alloys.

Table 4.11. Comparison of Pitting Resistance of Silicon-containing Alloy with Stainless Steels. (Streicher, 1977).

	Pitting Corrosion					
	$KMnO_4$/NaCl [b]			$FeCl_3 \cdot 6H_2O$ [c]		
	RT [d]	50°C	75°C	90°C	RT	50°C
SP-2 [a]	R [e]	R	F [f]	–	R	F
Types 304, 316 and 316L		–	–	–	F	–
18Cr-2Mo(Ti)		–	–	–	F	–
28Cr-2Mo		R	F	F	R	F
28Cr-2Mo-4Ni(Nb)		R	F	F	R	F
29Cr-4Mo		R	R	R	R	R
29Cr-4Mo-2Ni		R	R	R	R	R

(a) Type 316L alloy with 2.5% silicon, 0.23% nitrogen and 0.033% carbon

(b) 2% $KMnO_4$ - 2% NaCl, no crevices (pH = 7.5)

(c) 10% $FeCl_3 \cdot 6H_2O$, with crevices (pH = 1.6)

(d) Room temperature

(e) No Pitting

(f) Failed by pitting and/or crevice corrosion.

In the development of the SP-2 alloy, Streicher found that silicon provided the greatest resistance to pit initiation in 0.1N NaCl, being better than molybdenum. While silicon improved resistance to pit initiation, it could not be used alone to decrease pit propagation because it did not have much effect on passivation. The best combination was obtained by adding molybdenum since this element had a very beneficial effect on the passivation characteristics of the alloy. Sea-water exposure tests confirmed the results of the accelerated laboratory and $FeCl_3$ immersion tests in that additions of silicon improve the pitting resistance of Type 316.

The susceptibility of these silicon-bearing austenitics to inter-
granular corrosion in boiling 65% HNO₃ was found to increase when
silicon was present in excess of 1%. The corrosion rate was 0.062
mm/month compared to 0.020 mm/month for Types 304 and 316 stainless
steels.

Lizlovs (1966) examined the effect of silicon (and molybdenum and
copper) on the anodic behaviour of a 17% chromium ferritic stainless
steel. The addition of 1% silicon to a 17% chromium-molybdenum steel
did not produce a significant change in the critical current density,
but it did lower the primary passivation potential relative to the
silicon-free alloys. Silicon, therefore, appears to participate in
the formation and stabilization of the passive-film, an effect which
is more pronounced for the 3% than the 1% molybdenum alloy. On the
other hand, the addition of silicon to the 3% molybdenum alloy is
detrimental as far as the active corrosion rate is concerned,
although no such effect was found for the 1% molybdenum alloy.

The publications of Tomashov et al. (1964) and Biefer (1970) both
showed that silicon had a beneficial effect on resistance to pitting.
According to Tomashov et al., increasing silicon decreased the
corrosion rate of an 18Cr-14Ni alloy in FeCl₃ (Figure 4.3). The
pitting potential in NaCl increased above that for the base alloy
when the silicon content exceeded about 4% (Figure 4.4). Polariza-
tion measurements by Biefer on a Type 430 steel showed that silicon
increased the pitting potential in 0.5N NaCl, in fact producing a
somewhat better effect than vanadium (+531 mV for 1.78% silicon
compared to +468 mV for 2.18% vanadium). Brigham and Tozer (1974)
confirmed this effect of silicon at the 1.5% level in increasing the
pitting potential of an 18% chromium austenitic stainless steel.

4.5.2.   Stress-Corrosion Cracking.   Silicon appears to improve the
resistance of high-strength steels and austenitic stainless steels
to stress-corrosion cracking, but little is known regarding its
effect in ferritic stainless steels. Bond and Dundas (1968) found
that silicon did not change the time to cracking (or no cracking)
of various ferritic stainless steels in boiling MgCl₂, and concluded

that its effect was negligible in amounts up to 1%.

The effect of silicon in austenitic stainless steels is better
documented, and summarized in the paper by Hanninen (1979). Silicon
up to about 0.8% has little effect but higher levels (1.5 to 2%)
markedly improved the cracking resistance. One way in which it
influences cracking is to act synergistically with phosphorous to
reduce the detrimental effects of the latter. It has been concluded
that resistance to cracking of 2% silicon austenitic stainless
steels is not obtained by the addition of silicon alone, because
silicon does not sustain the resistance to cracking unless it
coexists with 0.045% or more solute carbon. Thus, silicon may lose
its positive effect resulting from sensitization when carbon
precipitates as a carbide, e.g. during welding.

4.6.   Copper

Copper itself has good resistance to corrosion by cold, dilute, non-
oxidizing and non-aerated acids, but not to the hot acids. Copper is
added to nickel-based alloys (e.g. Monel) and has been considered as
an alloying element in stainless steels (e.g. Carpenter 20Cb-3)
specifically to improve resistance to H_2SO_4.

The two limitations to the amount of copper that can be added to
stainless steels are fabrication problems (hot-shortness above about
2%) and susceptibility to stress-corrosion cracking. Copper has a
limited solubility in ferrite (1.4%) compared to austenite (8%).

In passivation experiments in H_2SO_4 (Lizlovs, 1966), the addition of
2% copper to a 17Cr-1Mo alloy decreased the critical current density
for primary passivation significantly, but proved detrimental to
passive film stability. In contrast, 2% copper added to a 17Cr-3Mo
alloy produced only a small decrease in the critical current density,
but greatly enhanced the passivity of the alloy.

The effect of copper has been examined in high-chromium superferritic
stainless steels in an attempt to obtain improved corrosion resistance

(Lennartz and Kiesheyer, 1971). At the 0.5% level, copper did not induce susceptibility to stress-corrosion cracking in 28Cr-2Mo-Ni alloys. Bond and Dundas (1968) found that copper up to 2% caused cracking in both commercially-and vacuum-melted 17Cr-Mo alloys in MgCl$_2$. For combinations of copper and nickel in 18Cr-2Mo-Ti alloys, only those alloys which showed the following relationship were found to be immune to stress-corrosion cracking in MgCl$_2$: %Ni + 3(% Cu)<0.9% (Steigerwald et al., 1977).

One of the few commercially available copper-containing stainless steels is Carpenter 20Cb-3 a 20Cr-34Ni-2.5Mo-3 alloy. Originally this alloy contained 29% nickel but was found to undergo stress-corrosion cracking in H$_2$SO$_4$ in the concentration range 20 to 80%. This cracking was attributed to the cathodic action of copper, and the problem was solved by increasing the nickel level from 29 to 34%.

4.7. Titanium and Niobium

These elements are added to ferritic stainless steels as stabilizers to combine with carbon and so prevent the precipitation of chromium carbide which leads to chromium dep.tion adjacent to the grain boundaries and hence susceptibility to intergranular corrosion. Titanium-stabilized alloys are not immune to intergranular corrosion in very strong oxidizing solutions due to dissolution of titanium carbide or an "invisible" sigma phase such as that encountered in Type 316L stainless steel   (Demo and Bond, 1975).

Titanium and niobium are somewhat detrimental to the pitting resistance of stainless steels, especially when either element is present in excess of stabilization requirements (Szklarska-Smialowska, 1971; Tomashov et al., 1964; see also Table 4.7). When in the correct amount for stabilization, however, both elements may have a beneficial effect on pitting (Lizlovs and Bond, 1969). Both elements have little effect on the passivation of stainless steels, being slightly beneficial (Tomashov and Chernova, 1967) or detrimental.

5.   EXPERIMENTAL PROCEDURE

5.1.   Selection of Experimental Alloys

The main advantage in adding molybdenum to a ferritic stainless steel,
such as Type 444, is to improve the resistance to pitting corrosion;
molybdenum at the 2% level has very little influence on the mechanical
properties. The carbon and nitrogen contents of Type 444 are low in
comparison to conventional ferritic stainless steels such as Type 430
in order to improve the mechanical properties, but the alloy neverthe-
less has limitations as far as welding and toughness, especially in
thick sections, are concerned. As a result, the commercial application
of Type 444 stainless steel is restricted to sections less than 2 mm
thick.

In the present study, while the emphasis is on replacing molybdenum
with vanadium mainly from the point of view of pitting corrosion
resistance, combinations with various other elements are examined in
an attempt to improve on the other inferior properties of ferritic
stainless steels, namely poor resistance to reducing acids,
susceptibility to weld decay and poor toughness. The literature
survey in the preceeding sections has revealed that vanadium has
a beneficial effect on the pitting resistance of stainless steels,
although it is not as effective as molybdenum. As regards corrosion
in general, it would appear that about 4% vanadium is capable of
replacing 2% molybdenum in stainless steels. This figure may be
reduced by some 2% if a favourable combination can be found with an
element such as silicon which is also known to improve the pitting
resistance of stainless steels. The silicon level would need to be
kept to less than 1.5% due to the possibility of embrittlement
occurring. Nickel has beneficial effects on both the mechanical and
corrosion resistance properties of ferritic stainless steels and is
therefore a worthwhile alloying element to consider. An upper limit
of 2% on the addition of nickel is necessary in order not to increase
susceptibility to stress-corrosion cracking and the tendency to form
austenite. Another element that has a beneficial effect in
atmospheric and reducing conditions is copper. Again, due to problems
such as hot-shortness and the possibility of stress-corrosion cracking,

the amount of copper should not exceed 1-2%.

Another factor to be considered in the development of a vanadium-bearing ferritic stainless steel is that of stabilization. Vanadium is a strong nitride and carbide former but would appear not to prevent sensitization unless present in excess of about 3%. The degree to which additional stabilization is required to obtain optimum benefits therefore needs to be investigated. It has been reported that a combined stabilizer addition, such as titanium plus niobium, provides the best results, but in keeping with the philosophy of the project, that is, only using materials that are not strategically limited in South Africa, titanium is the preferred choice. The use of a single stabilizer (apart from vanadium) is preferred, since the effect of its addition is more amenable to interpretation compared to multiple additions. Regarding the amount of stabilizer to be added, the general literature relationship of stabilizer = 7(C+N) was used (Demo, 1977). For a specified carbon plus nitrogen level of 125 ppm, the amount of stabilizer needed would be 0.09%.

The development of ferritic stainless steels containing vanadium was therefore examined from three viewpoints in this study:

1. Vanadium replacement of molybdenum.
2. Effect of stabilization with titanium (and niobium).
3. Nickel, silicon and copper additions.

The levels of carbon and nitrogen have a significant effect on both the mechanical and corrosion resistant properties of stainless steels. In order to reduce the detrimental effects of their presence to a minimum, as well as aid in the interpretation of the effects of the alloying elements, a maximum combined carbon plus nitrogen level of 125 ppm was specified in the preparation of the test alloys.

After careful consideration of the above factors, and bearing in mind costs and the maximising of useful information to be obtained, some 15 different alloy compositions were decided on. The compositions of the actual experimental alloys are given in Table 5.1.

Table 5.1.   Chemical Composition of the Experimental Alloys

| | % | | | | ppm | | | % |
	Cr	V	Ni	Ti	C	N	O	Other
1V	18.0	1.12	–	–	50	44	181	–
1V-Ti	18.0	1.09	–	0.07	50	67	41	–
1V-Ti-1Ni	17.9	1.05	0.99	0.09	50	45	64	–
2.6V	17.7	2.67	–	–	100	57	125	–
2.6V-Ti	17.7	2.47	–	0.07	30	80	147	–
2.6V-Ti-1Ni	18.1	2.61	0.95	0.10	40	84	133	–
4V	18.0	4.00	–	–	80	69	16	–
4V-Nb	17.8	4.10	–	–	70	80	24	0.09 Nb
4V-Ti	17.5	3.95	–	0.11	40	91	87	–
4V-Ti-1Ni	18.2	4.19	1.02	0.12	80	63	91	–
4V-Ti-1.5Ni	18.0	4.05	1.51	0.11	90	56	94	–
4V-Ti-2Ni	18.1	4.15	2.03	0.12	60	52	85	–
4V-Ti-1.5Ni-Si	18.0	4.09	1.50	0.12	100	68	93	1.48 Si
4V-Ti-1.5Ni-Cu	17.6	4.18	1.52	0.12	40	44	91	1.05 Cu
4V-Ti-Mo	17.9	4.17	–	0.11	60	61	92	0.86 Mo

Note: Maximum concentration of residual elements is as follows (%):
     Si – 0.04, P-0.02, S-0.008, Mo-0.5, others 0.02 (Al,Cu.Co,Ni, etc.)

5.2.   Preparation of Experimental Alloys

The experimental alloys were prepared from pure materials by vacuum
induction melting in the Department of Metallurgy at Sheffield
University in the United Kingdom. The chemical compositions given in
Table 5.1 are all within the limits specified by the author. After
casting as 75 mm square billets weighing 9 kg, the alloys were hot-
rolled in successive passes from 1050°C to a final thickness of 12 mm.
The five minute recrystallisation temperature was determined using
small specimens measuring 15 x 11 x 10 mm in size, which were heat-
treated for 10 minutes (5 minutes to reach specified temperature,

5 minutes at temperature). An average hardness value for these
specimens was plotted against temperature,and the recrystallisation
temperature determined (Table 5.2). The rolled plate material was
then annealed at the respective temperature for 30 minutes and water
quenched, and the specimens used for mechanical and corrosion testing
were cut directly from the plate material.

Table 5.2.   Annealing (= Recrystallisation) Temperature for
             Experimental Alloys

Alloy	Annealing Temperature (°C)
1V	825
1V-Ti	825
1V-Ti-1Ni	850
2.6V	825
2.6V-Ti	850
2.6V-Ti-1Ni	875
4V	825
4V-Nb	825
4V-Ti	
4V-Ti-1Ni	
4V-Ti-1.5Ni	850
4V-Ti-2Ni	
4V-Ti-1.5Ni-Si	
4V-Ti-1.5Ni-Cu	
4V-Ti-Mo	

5.3.   Test Programme

The test programme included detailed examination of the mechanical
and corrosion resistant properties of the alloys. Mechanical testing
involved determination of the tensile properties and impact ductile-
to-brittle transition temperature. Corrosion testing covered anodic
polarization in 1N H_2SO_4 and 0.1N NaCl, total immersion tests in

$FeCl_3$, HNO_3 and acetic acid solutions to determine corrosion rates, and intergranular corrosion testing using the Strauss test.

5.3.1.   **Mechanical Testing Procedures**. The tensile properties of the alloys were determined by the Department of Metallurgy, University of Sheffield, according to BS18: Part 2: 1971 using 5.6 mm diameter specimens. The gauge length for extensometry was 25 mm. Impact tests were performed by the author on a Karl Frank Type 580 Charpy tester with a maximum breaking energy of 294 Joules, using full-size (10 mm square) V-notched specimens to BS 131: Part 2: 1972. The specimens were cut with their length parallel to the rolling direction and the V-notch in the through-thickness side, and were heated in an oil container immersed in a thermostatically controlled water-bath for testing at various temperatures.

Vickers diamond hardness tests were carried out with a 30 kg load, with each result reported being the average of four determinations.

The fracture surfaces of the impact specimens were examined by scanning electron microscopy and the compositions of precipitates determined by X-ray analysis (EDAX).

5.3.2.   **Corrosion Testing Procedures.   Passivity Studies.**
Potentiodynamic polarization experiments were carried out in $1N\ H_2SO_4$ using the same apparatus described in ASTM Standard G5-72. The electrochemical measuring equipment comprised an Amel Model 551 potentiostat and ancilliary modules, together with a Hewlett-Packard 4060A, X-Y recorder. The test solution was prepared from analytical grade H_2SO_4 made up in distilled water, and deaerated during the entire test with bubbling argon. The test cell of one litre capacity was immersed in a thermostatically controlled water-bath maintained at $31 \pm 0.5°C$. All the potentials reported in this study are relative to the saturated calomel electrode (SCE).

The working electrode was in the form of a rod with an area of approximately 5 cm² and was secured, via a threaded rod, against a rubber O-ring. The test specimens were prepared by polishing to a 1000 grit finish with silicon carbide paper, cleaned ultrasonically in acetone

and alcohol, and then immersed immediately in the test electrolyte.
They were then cathodically activated at -560 mV for 5 min. in order
to remove any passive film that may have formed on the surface, and
subsequently allowed to stabilize for one hour. Polarization was
begun in the anodic direction at a scan rate of 200 μV/sec, from a
position 20 mV below the free-corrosion potential so that the
linear polarization technique could be used to determine the corrosion
rate. A slow scanning rate was chosen in order to more closely
approximate electrochemical equilibrium conditions during the
experiment. Scanning rates in the literature vary from 144 μV/s
(Bond et al., 1977) to a suggested 1000 μV/s (Man and Gabe, 1981).
All the experimental alloys were tested in duplicate.

Pitting Tests . Anodic polarization and immersion tests were carried
out to determine the susceptibility of the alloys to pitting corrosion.
The pitting potential was determined by anodic polarization in a
0.1N NaCl solution deaerated with argon, at three temperatures: 31,
59 and 81°C. The NaCl solution was prepared by dissolving analytical
grade NaCl in distilled water. The same apparatus and running procedure
as used for the passivity studies, with the except noted below, was
followed here. No attempt was made to mask off the area between the
specimen and the O-ring with the result that slight crevicing to
varying degrees was found during the experiments. The results should
therefore be regarded as absolute within this study only, but relative
with respect to other published results. The pitting potential was
taken at a value corresponding to a current density of 10 μA/cm², as
suggested by Truman (1978). Because of the poor reproducibility of the
results, from two to four polarization runs were necessary for each
alloy at a given temperature in order to obtain more realistic average
values. Statistics relating to reproducibility of the data are
recorded in the relevant table of results.

The protection potential was also determined in most of the runs
by reversing the scanning direction at a current density of 140 μA/cm²,
and the point noted at which the anodic curve was intersected.
However, because of the extreme variability of the results (probably
enhanced by the occurrence of crevicing at the specimen/O-ring

interface), the protection potential was not considered worth
recording. Following determination of the protection potential, one
specimen of each alloy was anodically polarized at a fast scan of
2 mV/sec to a current density varying from 10 - 50 μA/cm^2 in order to
induce significant pitting. These specimens were subsequently examined
under the scanning electron microscope to determine the nature of the
pitting.

In determining the anodic polarization characteristics in NaCl it was
found that the free-corrosion potential varied widely in replicate
determinations. Initially, cathodic activation was not carried out
but later, in an attempt to obtain a more reproducible free-corrosion
potential, activation at -850 mV was performed (no hydrogen was
evolved at this potential). About 30% of all runs were cathodically
activated and the results indicated that this led to more reproducible
(and more cathodic) values. Cathodic activation did not appear to
have any systematic effect on the pitting potential. In two cases
specimens were cathodically activated so that hydrogen evolution
occurred (-1000 and -1400 mV respectively), and this resulted in the
free-corrosion potential being raised (made more noble) to the extent
that it was not possible to determine the protection potential. For
this reason, a value of -850 mV was used for cathodic activation in
the experiments.

Resistance to pitting was also assessed using the ASTM Standard G48-76,
involving immersion in a 6% FeCl$_3$ solution at room temperature (23°C)
for 72 hours. The test solution was prepared from analytical grade
FeCl$_3$.6H$_2$O dissolved in distilled water. Specimens for the test
measured approximately 30 x 40 x 3 mm in size and were used in the as-
ground condition. They were cleaned ultrasonically in acetone and
ethanol, air-dried, weighed, and stored in a desiccator for subsequent
use. The same cleaning procedure was followed after the immersion test.
Susceptibility to pitting corrosion was assessed by measuring the
weight loss.

General Corrosion Tests. Immersion testing to assess general
corrosion was carried out according to the ASTM Standard G31-72 using

boiling solutions of concentrated HNO_3 (65%) and 3% oxalic acid. The test solutions were prepared from analytical grade reagents dissolved in distilled water. Flat specimens of the same size and prepared in the same way as for the $FeCl_3$ pitting tests were used. The immersion apparatus comprised a one litre round-bottomed flask seated in a heating mantle, with a double-walled condensor connected to a wide-mouthed ground-glass joint at the top of the flask. The specimen was placed in the test solution on a glass cradle with only one specimen tested in each flask.

The tests were run until the specimen appeared to have undergone significant corrosion, as indicated by discolouration of the test solution. This period varied from one to 16 days (recorded in the table of results). After removal from the test solution the samples were brushed under flowing water, then ultrasonically cleaned in acetone and ethanol, dried, and finally weighed to determine the weight loss.

A relative assessment of the corrosion rate in 1N H_2SO_4 was also made using the method of linear polarization. The slope of the polarization curve within 10 mV of the free-corrosion potential was determined and using average literature values for the cathodic and anodic Tafel slopes of 110 and 80 mV/decade (ASTM G59-78, and Lizlovs, 1966), the corrosion rate was obtained by substitution in the Stern-Geary formula:

$$i_{corr} = \frac{\beta_a \, \beta_c}{(2.3) \, (\text{slope}) \, (\beta_a + \beta_c)}$$

where β_a = anodic Tafel slope

β_c = cathodic Tafel slope.

Intergranular Corrosion Testing. Heat-treated and as-annealed specimens were tested in a $Cu/CuSO_4/H_2SO_4$ solution according to the Strauss test (ASTM, A262-75, Practice E). The test solution was prepared by dissolving analytical reagent grade $CuSO_4 \cdot 5H_2O$ and H_2SO_4 in distilled water. Electrolytic grade copper wire pieces covered the

test specimens completely during the experiment. Heat-treatment to
sensitize the alloys involved heating at 1150°C for one hour,
followed by water quenching. The test specimens measured
approximately 2.6 x 8.4 x 66 mm in size and were prepared in the
same way as for the immersion tests. Both sensitized and as-annealed
specimens of the same alloy were tested in the same flask (apparatus
as for immersion tests). After immersion in the boiling test
solution for 24 hours, the specimens were removed and cleaned as
for the immersion tests. Following cleaning, the specimens were
bent through 170°C over a 3 mm diameter shaft using a hydraulic press
and the apparatus designed by the author (see Appendix for details).
They were then examined under the electron microscope for evidence
of intergranular cracking.

The Strauss test is recommended by Streicher (1978) for the testing
of low - interstitial ferritic stainless steels. Time did not permit
the use of the other recommended method for these types of alloys,
namely the ferric sulphate and sulphuric acid test.

6. RESULTS AND DISCUSSION

6.1. Microstructure

Optical microscopic examination of the experimental alloys showed that
they were composed of ferrite only. Etching in Beraha's solution
(Beraha, 1966) revealed the nature of the grain boundaries and the form
and distribution of the precipitates. Table 6.1 shows that the Fe-Cr-V
alloys have the largest and most variable grain size. (It is possible
that the 18Cr-4V alloy, which has the largest grain size, is not fully re-
crystallised). Stabilization of the alloys with titanium is found to
decrease the grain size in all cases, but interestingly this does not
occur for niobium stabilization.

The precipitates visible under the optical microscope vary from small,
irregular to largish square-shaped types up to 0.005 mm across. The
last, which are present in all the alloys except th 18Cr-4V and 18Cr
18Cr-4V-Nb alloys, typically show a darker core an: ;:· ondary precipi-
tation around the edge. (Figures 6.1 and 6.2). Comparison of these
precipitates with those illustrated in other publications (e.g.
Pollard, 1974), indicates them to be nitrides or carbonitrides. The
amount of precipitation is found to vary according to the presence of
titanium and the degree of alloying. Stabilization with titanium
increases the amount of precipitation and the addition of alloying
elements increases this precipitation even further.

Optical microscopic examination has not revealed unambiguously whether
or not grain boundary precipitation is present, and transmission
electron microscopy seems necessary to clarify this point. Photographs
in publications (e.g. Abo et al., 1977) showing the presence or absence
of grain-boundary precipitates in low-interstitial ferritic stainless
steels are not always convincing to the author.

6.2. Mechanical Properties

6.2.1. Tensile Properties. The tensile properties of the experimental
alloys are listed in Table 6.2. Shown for comparison in the same Table
are some values for the commercial stainless steels, Types 316L, 436
and 444.

Table 6.1.   The Variation of Grain Size and Precipitate Content
             with Composition in the Experimental Alloys

Alloy	ASTM Grain Size	Precipitate Content (Relative)[a]
1V	1-4	Very few
1V-Ti	3-4	Few
1V-Ti-1Ni	4	More than previous two
2.6V	1-4	Few (more than 1V)
2.6V-Ti	4	Few (more than 2.6V)
2.6V-Ti-1Ni	3-4	Fair number (= 1V-Ti-1Ni)
4V	1	Very few
4V-Nb	1-4	Very few
4V-Ti	3-4	Fair number
4V-Ti-1N	3-4	Fair number (<4V-Ti)
4V-Ti-1.5Ni	3-4	"
4V-Ti-1Ni	4	"
4V-Ti-1.5Ni-Si	3	"
4V-Ti-1.5Ni-Cu	3	"
4V-Ti-Mo	3	"

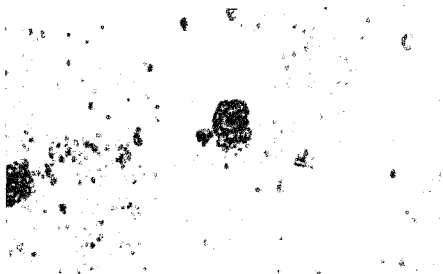(a) Data from optical microscopy

Figure 6.1. Typical large, square-shaped precipitate found in all the experimental alloys (except 4V and 4V-Nb alloys) showing secondary precipitation around the edge. Probably a nitride or carbonitride. (Etched, x600)

Figure 6.2. Rarer type of precipitate, probably titanium nitride. (Etched, x600)

Table 6.2. Tensile Properties of the Experimental Alloys Compared
to Other Stainless Steels.

Alloy	Yield Strength[a]	UTS[a]	% Elongation	% Red in Area	Hardness (VPN)
1V	288.6	324.0	35	85	150
1V-Ti	229.8	374.1	24	81	132
1V-Ti-1Ni	292.5	413.1	23	85	150
2.6V	268.9	419.2	20	83	151
2.6V-Ti	261	402.6	27.5	75	143
2.6V-Ti-1Ni	305.6	420.7	24	81	154
4V	339.3	469.1	22	58	159
4V-Nb	312.4	462.6	25	83	164
4V-Ti	280.0	419.2	24	83.5	150
4V-Ti-1Ni	342.5	463.2	21.5	82	156
4V-Ti-1.5Ni [b]	383.4	474.3	20.5	82	168
4V-Ti-2Ni	371.7	482.5	29	83	171
4V-Ti-1.5Ni-Si [b]	466.6	571.4	17	75	211
4V-Ti-1.5Ni-Cu [b]	421.6	501.4	28	80	181
4V-Ti-Mo [b]	311.2	458.7	22	78	171
Type 436 [c]	365	531	23	-	-
Type 444 [c]	360	515	29	-	-
Type 316 [c]	234	558	55	-	-

[a] MPa. Vanadium-bearing alloys accurate to $\pm$ 0.1 MPa. Yield strength corresponds to 0.2% proof stress.

[b] Specimens broke outside gauge length.

[c] From Climax Molybdenum and NACE Corrosion Engineers Reference Book (1980).

The tensile strength and percentage elongation values of the vanadium-bearing alloys are lower than for the austenitic Types 304 and 316, while the yield strength is higher. These trends, which are due to the work-hardening effect of nickel in the austenitic stainless steels, are similar to those found for ferritic stainless steels in general. The following general conclusions regarding the effect of other alloying elements can be inferred from Table 6.2:

    (i)   stabilization reduces the strength and has a variable effect on ductility which is lowered at the 1% vanadium level, but raised at the 4% level. Niobium is more beneficial than titanium, producing higher strength values and improving the ductility.

    (ii)   nickel raises the strength (in the stabilized condition) but reduces the ultimate tensile strength – yield strength ratio.

    (iii)   increasing nickel at a constant vanadium level, increases the strength and the ductility.

    (iv)   silicon increases the strength considerably but reduces the ductility.

    (v)   copper and molybdenum increase the strength. Molybdenum reduces the ductility slightly, but copper has a negligible effect.

The data do not show any dramatic or unexpected trends. Since the carbon and nitrogen levels vary within a narrow range, the trends shown can be ascribed largely to the effect of alloy elements.

The introduction of substitutional elements such as molybdenum, silicon, copper, nickel and vanadium into the ferrite phase is known to increase the strength, with the intensity of this solid-solution strengthening effect being dependent on the solute atom size. Of these elements, vanadium is closest to iron in atomic size and is the only one of these elements forming a continuous series of solid solutions with ferrite. Many substitutional elements react with interstitial solutes to form precipitates, such as TiC and TiN, which tend to decrease the overall solid-solution strengthening effect, but this may be offset by the

introduction of precipitation hardening.

The microscopic data do not reveal excessive precipitation in any of
the Fe-Cr-V alloys. Nunes (1966) has studied the effect of vanadium
on the tensile properties of pure iron (C + N + O = 100 ppm) and finds
an inversion in the strength at a vanadium concentration of 1%. In the
alloys here, this dip in strength appears to be pushed to the 2.6%
level. These results could be explained either by the partial removal
of nitrogen from solution by precipitation (the 2.6V alloy in fact
shows more precipitates than the 1V and 4V alloys; Table 6.1) or by
the association of vanadium and nitrogen atoms in solid-solution with
a consequent decrease in the rate of migration of nitrogen to
dislocations. Vanadium is known to form nitrides much more easily
than chromium in steels. It seems probable that the effect of
vanadium is first to remove nitrogen and then carbon from solid-
solution. Dijkstra and Sladek (1953) found internal friction evidence
for the association of vanadium and nitrogen atoms in solid-solution,
so it is possible that vanadium in solution could also have some
effect in retarding the strengthening effect at the 2.6% level. It
should be noted that solid-solution interactions between vanadium (and
molybdenum and chromium) and carbon have not been observed in iron
(Wert, 1952). An alternative explanation for the dip in strength at
the 2.6% vanadium level could be that (detrimental) precipitation
phenomena reach a maximum at this level whereas at the 1 and 4%
vanadium levels solid-solution hardening is dominant.

In contrast to the decrease in strength at the 2.6% vanadium level
reported here, the data of Climax Molybdenum show that strength increases
continuously with increasing vanadium at the 1, 2 and 3% vanadium
levels (Table 3.1). Variation in the proportion of different
precipitate types such as VN, V_4C_3 and $Cr_{23}C_6$ probably also influence
the relative variation in strength with vanadium concentration.

The addition of a strong stabilizer, such as titanium or niobium,
appears to reduce strength as a result of excessive precipitation.
Odesskii et al. (1978) examined the effect of vanadium in a stabilized
17% chromium stainless steel (800ppm carbon)   and found that titanium

was present as stable carbides, while vanadium occurred mainly in the
alpha-solid solution. It was also found that vanadium improved
ductility by reducing the amount of brittle transformation products,
such as martensite.

Titanium and niobium are the strongest carbide and nitride formers of
the various elements considered here. Their carbides and nitrides
form a continuous series of solid- solutions but, because of the
greater stability of the nitride, there is probably a tendency for
titanium nitride to precipitate first from the steel. In this respect
it is similar to vanadium. While titanium (and niobium) are grain
refiners and could thus be expected to increase strength, precipitation
phenomena in most cases obscure and override this effect in stainless
steels. The greater strengthening effect of niobium compared to
titanium is probably related to the different shape of precipitates
these two elements form, rather than to a difference in grain
refining properties. As pointed out by Steigerwald et al. (1977) the
precipitates in niobium-stabilized, ferritic stainless steels are
relatively small and finely dispersed, while those in titanium steels
are fairly coarse and angular. A similar conclusion is reported by
Pollard (1974) who considers that precipitate morphology rather than
chemical composition is the important factor in determining ductility.
Scanning electron microscopy examination of impact fracture surfaces
(Section 6.3) in fact show that precipitates are much smaller in the
niobium-stabilized alloy than in the case for titanium-stabilization.

Tensile properties are influenced by grain size as well as alloy
content. Decreasing grain size should lead to increased strength but
this effect can be obscured by precipitation phenomena. The data
in Table 6.1 indicate a general decrease in grain size with increase
in combined alloy content related mainly, however, to titanium-
stabilization. Plumtree and Gullberg (1974) have examined the effect
of interstitial elements on the mechanical properties of 25% chromium
ferritic alloys and find no detectable dependency of yield strength
on grain size.

6.2.2. Impact Properties. Charpy V-notch impact transition temperature curves for the experimental alloys are shown in Figures 6.3-6.5. Table 6.3 lists the transition temperature corresponding to an impact energy of 100 Joules, as well as the room temperature (20°C) impact values found for transverse sections obtained by the University of Sheffield. Single curves have been drawn as a best fit to the experimental points in Figures 6.3 - 6.5, but many more points would probably show a spread as is found by other authors for low-interstitial alloys (Steigerwald et al., 1977). This spread would account for the higher impact values found by Sheffield University for alloys 4V and 4V-Nb. Nevertheless, the curves are interpreted as means with an estimated error of ± 4°C and differences exceeding the error are regarded as indicating alloying trends.

In none of the alloys was it possible to obtain an upper shelf energy value because of the limited capacity of the Charpy tester. Upper shelf values are not reported in the literature for full-size Charpy V-notch determinations of low-interstitial ferritics, but are known to exceed 320 Joules as shown for Type 444 alloys (Steigerwald et al., 1977).

Examination of the impact data shows some very interesting trends. The most important factors influencing the results are alloy composition and stabilization, with other factors such as grain size and inter-stitial content appearing to be less important.

Vanadium. An increase in vanadium decreases the impact transition temperature significantly, to the extent that at a level of 4% the alloy is ductile within a few degrees of room temperature. (In fact, as noted, the 4V and 4V-Nb alloys tested by the University of Sheffield were ductile at room temperature , 20°C; Table 6.3). The beneficial effect of vanadium in low-interstitial 18% chromium ferritic stainless steels has been noted by Aslund (1977) and Climax Molybdenum (Tables 3.1 and 3.3). In contrast, however, they found that a low vanadium level of 1% was also very beneficial, giving a transition temperature of below zero.

Figure 6.3. Transition temperature curves for full-size Charpy V-notch impact specimens of 18% stainless steels, with and without stabilization. Stabilized and unstabilized Type 444 shown for comparison (Steigerwald et al., 1977).
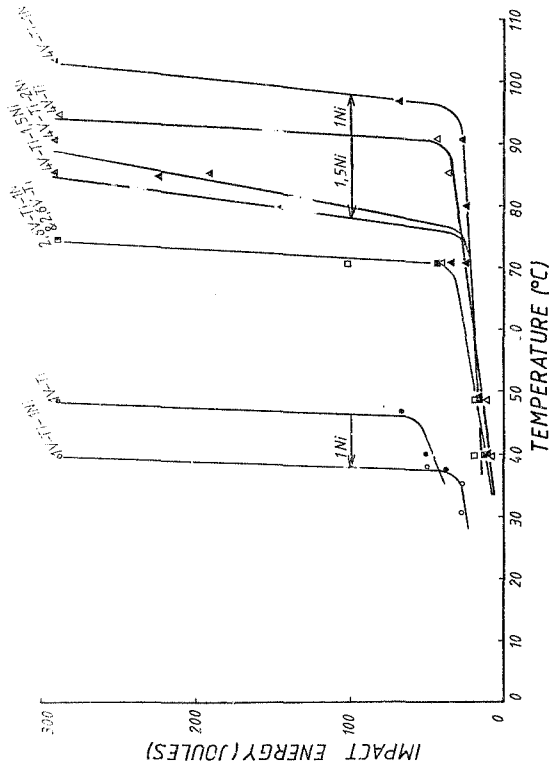
Figure 6.4.   Transition temperature curves for full-size Charpy V-notch specimens of 18%
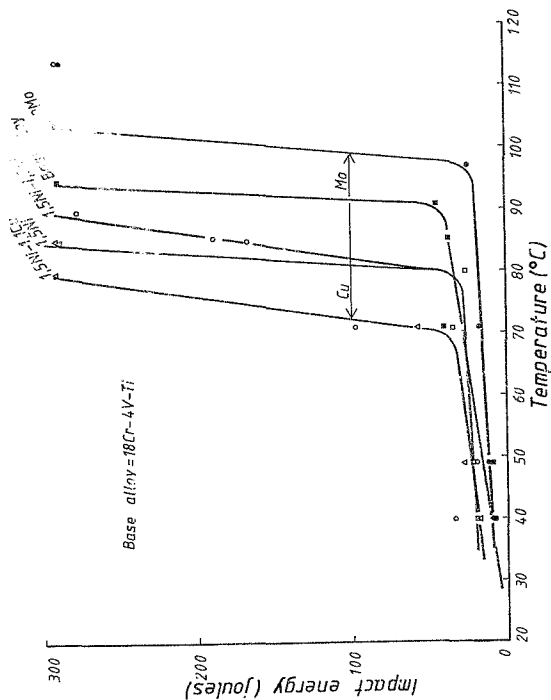Cr-V-Ti stainless steels, showing the effect of adding nickel.

Figure 6.5.   Transition temperature curves for full-size Charpy V-notch impact specimens of 18% Cr-V-Ti stainless steels showing the effect of alloying with Cu, Si, and Mo.

Table 6.3. Impact Transition Temperature and Energy Values for
the Experimental Alloys

Alloy	Transition Temp(°C) at 100 Joules [a]	Impact Energy at 20°C (Joules) [b]
1V	85.5	12.2
1V-Ti	46.5	13.6
1V-Ti-1Ni	38	23.0
2.6V	70.5	9.1
2.6V-Ti	71.5	9.5
2.6V-Ti-1Ni	71.5	19.0
4V	27	233.2
4V-Nb	32.5	252.2
4V-Ti	92	10.8
4V-Ti-1Ni	98	9.5
4V-Ti-1.5Ni	76	14.9
4V-Ti-2Ni	80	10.8
4V-Ti-1.5Ni-Si	84	10.8
4V-Ti-1.5Ni-Cu	74.5	13.6
4V-Ti-Mo	98	8.1

[a] Values from Figures 6.3-6.5. For comparison, the transition
temperature for Type 316 is -516°C and Type 444, +25 to +75°C (FATT).

[b] As determined by the University of Sheffield on 10 mm transverse
specimens (V-notch in through-thickness side).

SEM-EDAX analysis of the ductile fracture surface shows that the
alloys contain a fair number of very small precipitates ranging in
size up to 4 μm. Their shapes vary from irregular to rounded and
rectangular. EDAX analysis of five of the largest precipitates gave
the following results: Al-V-Cr rich (1% vanadium alloy); Ti-V-Cr and
Al-P-Cl rich, the latter twice (2.6% vanadium alloy); Al-rich (4%
vanadium alloy). Titanium in the 2.6% vanadium alloy is a contaminant,
since the alloys were not titanium-stabilized. SEM micrographs
illustrating general surface features and the nature of precipitates
are shown in Figures 6.6 to 6.10 (Figure 6.8 shows the EDAX
determined composition of the precipitate in Figure 6.7). A
characteristic of the Fe-Cr-V alloys is the absence of sizeable
precipitates (compared to their titanium-stabilized counterparts,
Figures 6.12 to 6.14) although closer examination shows many very
small precipitates, 0.5 μm or less across. The 4V alloy shows a
characteristic cellular structure very similar to the 4V-Nb alloy
(Figure 6.11) which also has a very low impact transition temperature.

The optical and electron microscopy data are insufficient to draw
conclusions regarding just how vanadium acts to lower the transition
temperature. Conjecturely, considering the data of Shaw and Quarrell
(1957), $Cr_{23}C_6$ may be the dominant precipitating phase in the low
(1%) vanadium alloy whereas V_4C_3 is predominant at high vanadium
levels and is proving beneficial. A low vanadium concentration of
1% is probably sufficient to combine all the nitrogen in vanadium
nitride, but is insufficient to combine with all the carbon. As noted
previously, vanadium occurs both in solid-solution and as a precipitate
in stainless steels. Any uncombined carbon would then be free to com-
bine with chromium to form grain boundary $Cr_{23}C_6$ which can prove detri-
mental to the impact properties. At higher vanadium levels progressively
more of the carbon is combined as vanadium carbide (probably V_4C_3) or a
Cr-V-Fe sigma phase, which occurs within the alpha matrix and is bene-
ficial to toughness (compared to $Cr_{23}C_6$). In conjunction with this
effect is the action of vanadium in reducing the coarseness of any
$Cr_{23}C_6$ precipitates that may be present which would improve the impact
properties further. In his study on the effect of vanadium in an
austenitic stainless steel, Silcock (1973) purposely kept the V/C ratio

Figure 6.6.   SEM micrograph of ductile fracture surface of 1V alloy
              showing absence of precipitates (many very small
              precipitates are visible).

Figure 6.7.   SEM micrograph showing detail of a precipitate from
              ductile fracture surface of the 1V alloy.

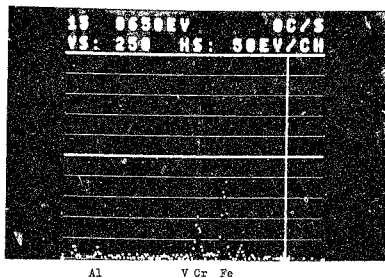Figure 6.8. SEM-EDAX analysis of precipitate shown in Figure 6.7. (Cr-V-Al rich).

Figure 6.9. SEM micrograph of ductile fracture surface of 2.6V alloy showing very small scattered precipitates.
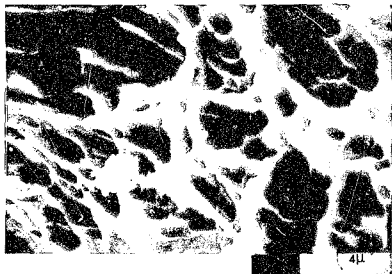
Figure 6.10. SEM micrograph of ductile fracture surface of 4V alloy showing cellular structure and very small precipitates.
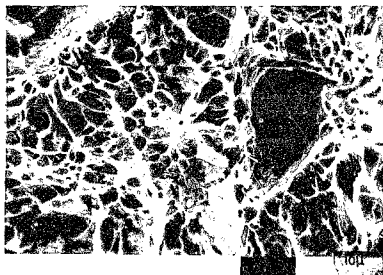

Figure 6.11. SEM micrograph of ductile fracture surface of 4V-Nb alloy showing cellular structure.

high (greater than that in V_4C_3) to restrict $M_{23}C_6$ gain boundary
formation.   The precipitates in the present alloys are not
pure phases and contain a mixture of the elements iron, chromium and
vanadium, thus $(Cr, Fe, V)_{23} C_6$, to varying degrees. Shaw and
Quarrell (1957) have noted that chromium and iron are virtually inter-
changeable in the carbides formed in austenitic stainless steels.
Transmission electron microscopy would seem necessary to determine
the extent of grain boundary and matrix precipitation and hence its
relation to impact properties.

Stabilization. The effect of stabilization with titanium is to
exactly reverse the trend found for the Fe-Cr-V alloys, with the 1V-Ti
alloy showing a much lower transition temperature (47°C) than the 4V-Ti
alloy (92°C)(Table 6.3). Significantly, niobium has only a slightly
detrimental effect in raising the transition temperature of the 4V
alloy by some 5°C. Stabili   titanium, especially when the
element is present in excess   to increase the transition
temperature of stainless steels   Table 2.3),but niobium in con-
trast actually lowers the transition temperature when present in the
correct proportion (Figure 2.6).

Scanning electron microscopy confirms the optical microscopy result
that titanium-stabilization leads to an increase in the number of
precipitates found in the alloys. The precipitates showed the same
shapes as found in the unstabilized alloys, but were much larger on
average (about $2\mu m$) with a slightly larger maximum size, up to $6\mu m$.
EDAX analysis showed a precipitate in a 1V alloy to be Ti-V rich, and
another in a 4V alloy to be Al-1i-V rich. In contrast to the
titanium-stabilized alloys, the alloy containing niobium showed much
smaller precipitates, less than $1\mu m$ in size, which were not amenable
to identification by X-ray analysis. Figures 6.11 to 6.16 show SEM
features of the ductile fracture surfaces and includes the EDAX
determined composition of two precipitates. From a comparison of the
SEM micrographs for the titanium-stabilized and unstabilized alloys,
the following observation can be made: in all the alloys titanium-
stabilization increases the amount of precipitation but whereas this
produces a drop in the impact transition temperature of the 1V alloy,
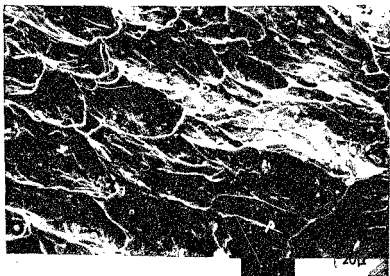
Figure 6.12 SEM micrograph of ductile fracture surface of 1V-Ti alloy showing many scattered precipitates. (Compare to Figure 6.6).

Figure 6.13. SEM micrograph of ductile fracture surface of 2.6V-Ti alloy showing many scattered precipitates. (Compare to Figure 6.9).
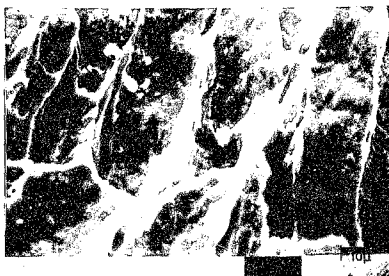
Figure 6.14. SEM micrograph of ductile fracture surface of 4V-Ti-1Ni
alloy showing many scattered precipitates. (Contrast
with Figure 6.10).

Figure 6.15. SEM-EDAX analysis of tear-drop precipitate near centre of
Figure 6.14. Dots represent the base alloy, and the
grey area the precipitate (Ti-V rich).

Ti V Cr Fe

Figure 6.16. SEM-EDAX analysis of precipitate in 4V-Ti-1.5Ni-Cu
alloy. Dots represent the base alloy, the gray
area the precipitate (Ti-V rich).

it results in a considerable increase in the transition temperature
of the 4V alloy. In the 2.6V alloy, stabilization has little effect on
the transition temperature. Clearly, the amount of precipitation is not
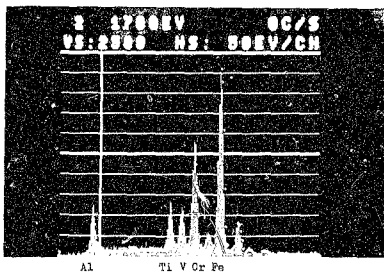a controlling factor in determining the impact properties of the alloys.

Regarding the composition of the precipitates, EDAX data indicate that
those in the Fe-Cr-V alloys are chromium- and vanadium-rich, while
those in the titanium-stabilized alloys are titanium- and vanadium-rich.
Those in the former alloys are probably carbides and nitrides, and in
the latter alloys nitrides and carbonitrides.

The different impact results found for the titanium- and niobium-
containing alloys appear to be related to precipitate morphology: those
in the case of niobium are very small and have little effect, whereas
those in the titanium alloys are larger and thus detrimental. This
difference has been noted by Steigerwald et al. (1977) who also found
that the titanium-containing precipitates were more angular. Abo et
al. (1977) studied the different effects of niobium and titanium in
low-interstitial ferritic stainless steels, and found that niobium
improved toughness properties when in the correct proportion in
relation to carbon and nitrogen (Nb = 8-10(C+N)). Excess (or too
little) niobium proved detrimental to toughness. According to the
authors, the effect of niobium was to decrease the amount of grain
boundary precipitate. In the same study titanium was found to increase
the transition temperature markedly and, in contrast to niobium, con-
tinuously. Titanium was considered to inhibit grain boundary precipi-
tation of carbonitrides but nevertheless had a detrimental effect in
that precipitates in the matrix were acting as crack iniation sites in
the same way that grain boundary precipitates would. The titanium-
stabilized alloys contained more precipitates than in the case for
niobium, and they were considerably larger and more angular. Their
composition was shown to be mainly titanium nitride. A comparison of
the results obtained here with those found by Abo et al. (1977) and
Steigerwald et al. (1977) show many similarities, and the same
conclusions appear applicable. The amount of titanium and niobium in
the experimental alloys are within the limits specified for low-inter-
stitial alloys, the stabilizer/(C+N) ratios being 6-9 and 6
respectively (Table 6.1) (Demo, 1977). Some authors report that an

.... of titanium is needed for effective stabilization (to prevent
.....granular corrosion) in ferritic alloys, but Abo et al. (1977) find
that the requirement is equal to or even *less than stoichiometric*
proportions for 19% chromium-2% molybdenum alloys containing less than
140 ppm combined carbon plus nitrogen. Clearly, excess titanium here is
not the reason for the titanium-stabilized alloy having poorer impact
properties than the alloy stabilized with niobium.

The trend in the impact data for the titanium-stabilized alloys is the
reverse of that for the unstabilized alloys. *The reason why titanium
is beneficial below, but detrimental above, a vanadium concentration
of 2.6% is not clear.* A synergistic effect appears to be present at
the lower vanadium level. Titanium is a strong carbide former and
would be expected to combine all the carbon and nitrogen in the
titanium carbonitrides and nitrides. If this was the case, then
vanadium would not be expected to form significant precipitation at
any concentration and is *largely confined in solid-solution*, apart
from a small amount present with titanium in the nitrides or
carbonitrides. It is possible that supersaturation of the alpha
matrix with vanadium has caused titanium to be excluded and to form an
increasing amount of grain boundary precipitation as the vanadium
level increases. In al most all cases of reduced toughness in ferritic
and other stainless steels, grain boundary or matrix precipitation is
found to be the *cause and it must therefore be concluded* in the
present study that some precipitating phase is responsible for the
deteriorating toughness which occurs with an increase in vanadium
concentration. There is no evidence of intergranular cleavage in
the brittle Charpy specimens and transmission electron microscopy
was necessary to resolve the problem.

Other Alloying Elements. Regarding the effect of adding 1-2% of other
alloying elements on the impact properties, nickel was found to be
......ble but on balance lowered the transition temperature, copper
.......ed the transition temperature by 4°C, and silicon and molybdenum
...ised the transition temperature by 6 and 28°C respectively.

Scanning electron microscopic examination of the ductile fracture

surface of the alloys containing these elements showed them to have as
many precipitates as the Fe-Cr-V-Ti alloys, with a similar morphology
and size range. Of the 14 precipitates analysed by EDAX, 11 contained
the titanium-vanadium combination and 6 contained aluminium. The
brittle fracture surfaces showed a dominant transgranular mode of
failure. (It should be mentioned that the precipitates on the fracture
surfaces of all the experimental al oys do not appear to be representa-
tive of the total precipitate population since 12 out of a total of 26
precipitates analysed from surfaces pitted in NaCl contained the
chromium-vanadium combination.)

The general improvement in toughness that nickel confers on ferritic
stainless steels has been reported in various publications. Bond et
al. (1977) examined the effect of nickel, molybdenum and copper on the
toughness of 25% chromium alloys and found nickel to be most effective
above a concentration of 2%, while variations in molybdenum from 2 to
4% and copper from 0.5 to 1% had a small effect only. The effect of
silicon in reducing the toughness in the present study is expected in
view of the tendency of the element to cause embrittlement in iron-
chromium alloys. In low-alloy steels, however, silicon is known to
improve the toughness (Tetelman and McEvily, 1967).

It appears that titanium stabilization has the dominant influence on
the impact properties of the experimental alloys, and other elements
such as nickel, silicon, copper and molybdenum are acting in
proportion to their concentration.

Grain Size. The grain size can have an important influence on the
mechanical properties of ferritic stainless steels but, as mentioned
in the section on tensile properties, precipitation phenomena can have
an overriding effect. This is also the case for the impact
properties. Increasing grain size should lead to decreasing toughness
for a given composition. In this study, most of the alloys with the
smallest grain size have the highest transition temperatures and
there is no discernable effect of grain size on toughness even
considering the varying composition of the alloys. Clearly, alloying
elements and particularly stabilizing elements are playing a more
important role.

Interstitial Elements.   In preparing the alloys an attempt was made to keep the interstitial element level as constant as possible; nevertheless, the total combined carbon, nitrogen and oxygen content ranged from 158 to 282 ppm with carbon varying from 30 to 100 ppm. These ranges are not large but probably contribute in some measure to the variations found in the mechanical properties. The greatest range was shown by oxygen, from 16 ppm in the 4V alloy to 181 ppm in the 1V alloy. Abo et al. (1977) have shown that an increase in oxygen from 100 to 200 ppm in 25Cr-3Mo alloys (C+N = 100-400 ppm) increased the impact transition temperature by 40°C. High oxygen levels could therefore be considered as contributing to the poor impact properties found for some of the alloys, e.g. 1V, 2.6V, 2.6V-Ti and 2.6V-Ti-Ni.

Carbon and nitrogen are well known to have a detrimental effect on the toughness of ferritic stainless steels. These elements vary by a factor of 3 and 2 respectively in the experimental alloys, with the combined carbon and nitrogen content ranging from 64 to 168 ppm. The variation in carbon content probably has more significance as far as the alloys are concerned since it is found that resistance to inter-granular corrosion at carbon plus nitrogen levels below 250 ppm is essentially independent of nitrogen. Davis et al. (1980) report that nitrogen in the range 35-176 ppm did not affect susceptibility to intergranular corrosion in niobium-stabilized 26Cr-1Mo alloys. The highest carbon contents of 100 ppm were found in the 2.6V and 4V-Ti-1.5Ni-Si alloys, but apart from having rather poor impact properties, neither alloy showed anomalous results compared to some of the other alloys.

6.3.   Corrosion Properties

6.3.1. Passivity in H_2SO_4.   The passive characteristics of the experimental alloys were examined by anodic polarization in deaerated 1N H_2SO_4. Potential and current density values for various points on the polarization curve are given in Tables 6.4 and 6.5 respectively, being chosen to illustrate trends such as the active, passive and transpassive ranges of the alloys. Entry and exit from the passive region is arbitrarily taken at a current density of 100 μA/cm² to

facilitate some measure of comparison with the results of other
research workers. It should be noted that the anodic polarization
results relate only to th- alloys tested and comparison with published
data must consider the exact experimental procedures adopted. A more
absolute comparison can be made with the published literature by
comparing the respective data for two standard stainless steels,
Types 430 and 316, the results for which are reported in Tables 6.4
and 6.5. Polarization curves illustrating the various alloying
trends are shown in Figures 6.17 to 6.21,and Figure 6.22 summarizes
the effects of the various elements.

Vanadium. An increase in vanadium from 1 to 4% in the 18% chromium
base alloy generally had a beneficial effect on passivation in
1N H_2SO_4. The primary passivation characteristics were improved
(e.g. critical current density lowered) and the potential range at a
current density of $100 \mu A/cm^2$ increased (Figure 6.17) However ,
vanadium was detrimental in that it significantly lowered the break-
down potential due to incipient breakaway of the transpassive region
(not to be confused with the normal transpassive transition that
occurs at high current densities, $4000 \mu A/cm^2$ in the results of
Biefer (1970) for Type 430 stainless steel). Biefer (1970) found that
the addition of up to 2.18% vanadium had a variable effect on the
passivation of Type 430 stainless steel : vanadium raised the critical
passivation potential, but lowered the critical current density and
the minimum current in the passive region.

The reason for vanadium lowering the breakdown potential could be
related to precipitation phenomena, although this is not evident in
the examination by optical and scanning electron microscopy. In
discussing the mechanical properties,it was suggested that vanadium
at the 2.6%V level would probably have combined all the nitrogen and
carbon in precipitate form,thus leaving more free vanadium in solid-
solution at the 4% level. This should have a generally beneficial
effect on passivity. Secondary peaks have been noted in the literature
in the passive region of austenitic stainless steels and are usually
related to dissolution of titanium carbide at the extremes of the
passive range where the passive film is least stable.

Table 6.4. Results of Anodic Polarization Measurements in
Deaerated 1N H_2SO_4 at 31°C.

Alloy	Ecorr	Ecp	Ep	Ea	Eb	E100[b]
			Potential	(mV)	versus SCE[a]	
1V	-498	-423	-263	+ 38	+720	-338/+895
1V-Ti	-492	-420	-300	+ 51	+808	-340/+966
1V-Ti-1Ni	-533	-440	-243	–	+761	-346/+982
2.6V[c]	-496	-435	-274	+ 24	+587	-344/+929
2.6V-Ti	-493	-434	-286	+ 42	+790	-345/+942
2.6V-Ti-1Ni	-535	-449	-280	–	+754	-333/+980
4V[c]	-512	-451	-292	+ 6	+451	-360/+966
4V-Nb[c]	-505	-450	-300	+ 10	+452	-360/+960
4V-Ti	-498	-440	-293	+ 38	+719	-368/+958
4V-Ti-1Ni	-538	-454	-328	–	+750	-381/+997
4V-Ti-1.5Ni	-540	-459	-327	–	+771	-377/+1006
4V-Ti-1Ni	-525	-461	-345	-302	+770	-387/+1018
4V-Ti-1.5Ni-Si	-523	-470	-353	-318	+770	-390/+960
4V-Ti-1.5Ni-Cu[d]	-451	-418	-136	-291/-11[e]	+780	(-3)/+977
4V-Ti-Mo	-547	-472	-324	-103	+788	-382/+1004
Type 430	-505	-411	-178	+ 53	+713	-220/+978
Type 444[f]	-501	-438	-326	- 54	+824	-371/+999
Type 316[g]	-311	-266	- 98	~	+8	-74/+70

[a] See Figure 6.22 for abbreviations

[b] E100 are the potentials corresponding to 100μ A/cm²

[c] Transpassive values, Eta/Etb : 2.6V, +831/+877; 4V,
     +703/+813; 4V-Nb, + 753/+813.

[d] With cathodic activation. Values without cathodic activation
     are : Ecorr = -292; Ecpp = -220; Eb = +855.

[e] Two secondary anodic peaks present. Neither present, however,
     without cathodic activation.

[f] Emery-polished, cold-rolled and annealed sheet. 18Cr-2Mo-Nb/Ta.

[g] Composition (%):Cr = 16.5, Ni = 10.31, Mo = 2.06, Ti = 0.2.
     C = 0.033, N = 0.0135.

Statistics: The percentage deviation from the mean for selected
potentials is as follows: Ecorr = ± 0.36% (range 0 - 2.04%),
Ep = ± 2.06%.

Table 6.5.   Results of Anodic Polarization Measurements in
              Deaerated 1N H_2SO_4 at 31°C.

Alloy	Current Density (μA/cm²)[a]				
	Icp	Ip	Ia	Ib	I min.
1V	36621	19.4	14.8	7.8	7.1
1V-Ti	21109	15.8	6.8	4.9	3.2
1V-Ti-1Ni	10087	15.5	–	2.9	1.6
2.6V[b]	19549	17.6	17.3	7.9	7.2
2.6V-Ti	17136	19.3	12.4	6.9	5.0
2.6V-Ti-1Ni	7405	8.3	–	3.2	1.7
4V[b]	10351	14.7	15.4	6.3	5.9
4V-Nb[b]	11021	14.7	14	5.8	5.2
4V-Ti	11287	14.7	12.9	6.3	5.0
4V-Ti-1Ni	4139	16.9	–	3.2	2.0
4V-Ti-1.5Ni	3211	7.9	–	3.4	1.4
4V-Ti-2Ni	2423	6.6	7.3	3.1	2.0
4V-Ti-1.5Ni-Si	2306	11.9	12.2	3.5	1.7
4V-Ti-1.5Ni-Cu[c]	85	2.3	5.4/129[d]	2.8	1.5
4V-Ti-Mo	3035	11.3	4.0	3.0	1.6
Type 430	18766	23.6	98	3.9	2.5
Type 444[e]	2314	16.7	13.9	4.3	2.0
Type 316	28.6	4.2	–	3.0	1.4

[a] See Figure 6.22 for abbreviations

[b] Transpassive values, Ita/Itb : 2.6V, 67.6/56.8; 4V,48/238;
     4V-Nb, 21.4/16.1

[c] With cathodic activation. Values without cathodic activation
     are : Icpp = 4.4; Ib = 4.4.

[d] Two secondary anodic peaks present. Neither present, however,
     without cathodic activation.

[e] Polished, cold-rolled and annealed sheet.

Statistics: The percentage deviation from the mean for Icp is

$\pm$ 2.63% (range 0.51 – 7.83%).
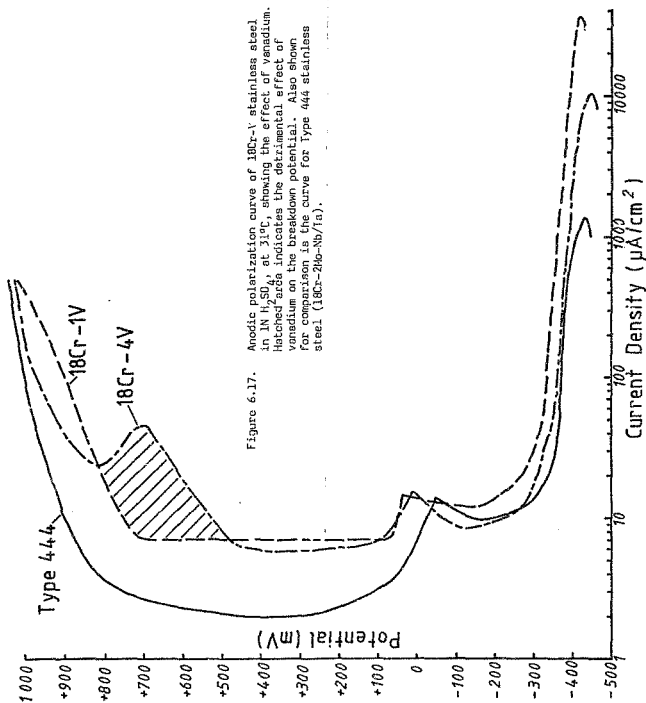
Figure 6.17. Anodic polarization curve of 18Cr-V stainless steel in 1N H_2SO_4, at 31°C, showing the effect of vanadium. Hatched area indicates the detrimental effect of vanadium on the breakdown potential. Also shown for comparison is the curve for Type 444 stainless steel (18Cr-2Mo-Nb/Ti).
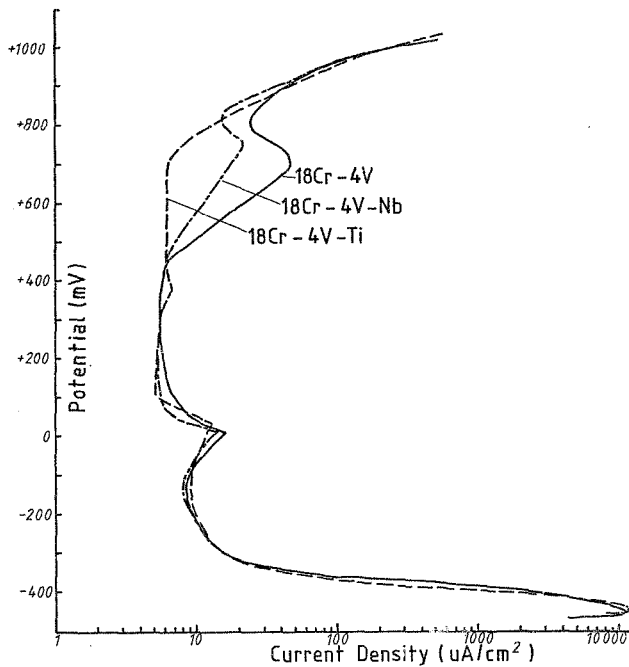
Figure 6.18. Anodic polarization curve of 18Cr–4V stainless steel in 1N H_2SO_4, at 31°C, showing the effect of stabilization with titanium and niobium.
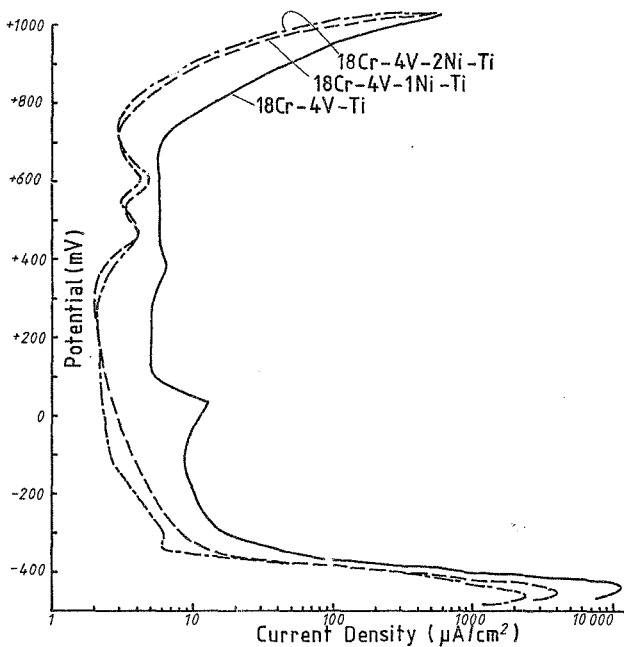
Figure 6.19. Anodic polarization curve of 18Cr-4V-Ti stainless steel in 1N H_2SO_4, at 31°C, showing the effect of adding nickel.
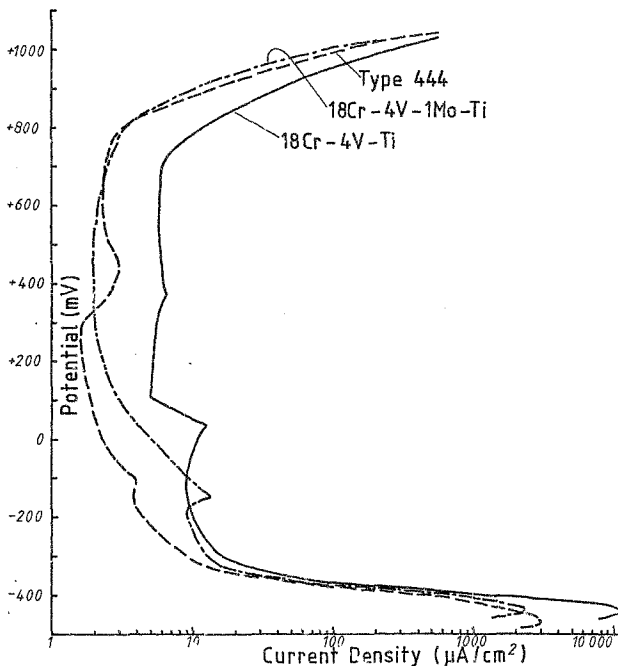
Figure 6.20   Anodic polarization curve of 18Cr-4V-Ti stainless steel in 1N H_2SO_4, at 31°C, showing the effect of adding 1% molybdenum. Shown for comparison is Type 444 stainless steel (18Cr-2Mo-Nb/Ta).
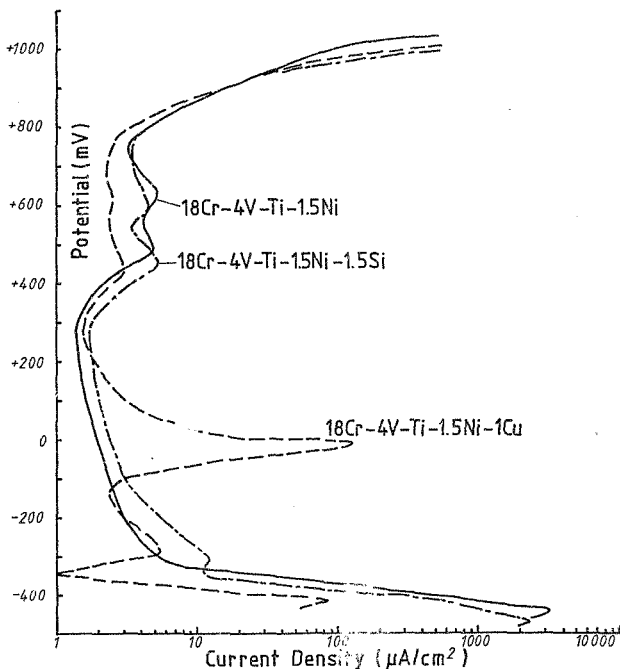
Figure 6.21. Anodic polarization curve of 18Cr-4V-Ti-1.5 Ni in 1N H_2SO_4, at 31°C, showing the effect of adding copper (1%) and silicon (1.5%). The large anodic peak at zero potential in the copper-containing alloy disappears when cathodic activation is not carried out prior to determination of the anodic polarization curve.
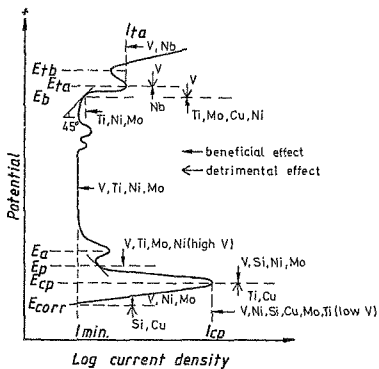
Figure 6.22. Generalized effect of alloying elements on the anodic polarization of 18Cr-V stainless steels in 1N H_2SO_4. (From this study).

A base alloy without vanadium was not examined in this study, but is
expected to have poorer passivation characteristics compared to the
vanadium-bearing alloy. The reason for the Type 430 alloy having a
lower critical current density compared to the low-interstitial
18Cr–1V alloy is largely related to carbon content. Wilde and Green
(1969) have shown that an increase in the carbon content significantly
reduced the critical current density in Types 304 and 316 stainless
steels.

The Fe-Cr-V alloys (and most of the other alloys in this study) show a
small second anodic polarization current maxima in the lower portion
of the passive region, approximately in the zero potential position
(Figure 6.17) A more pronounced peak in the same position is
frequently observed in commercially made stainless steels (e.g.
Type 430 and CF–8) and is ascribed to such factors as grain boundary
dissolution, the time delay between immersion and polarization; and
hydrogen oxidation for specimens pretreated at cathodic potentials for
significant periods. Cigada et al. (1978) and France and Greene
(1968) have shown that the size of this secondary peak depends on the
pre-polarization immersion period and the alloy composition. In the
present alloys, immersion period and cathodic activation are probably
the main factors accounting for the anodic peak. France and Greene
(1968) consider that nickel enrichment on the electrode surface,
enhanced by long pre-polarization exposure, high alloy corrosion rate
and high nickel content are the cause of the secondary peak. This
explanation is probably not a significant factor for the alloys
containing nickel in this study because they showed very small or non-
existent secondary peaks (Figure 6.21). In addition, the Fe-Cr-V alloys
contain negligible nickel (< 0.02%).

Titanium and Niobium. The most significant effect of adding 0.1%
titanium to the Fe-Cr-V alloy is to raise the breakdown potential and
thus eliminate incipient breakaway of the transpassive region
(Figure 6.18). Titanium and vanadium appear to combine synergistically
because the breakdown potential decreases only slightly with an
increasing vanadium level. Titanium had very little effect on the
remainder of the anodic polarization curve except to cause a slight
dip in the passive region.

In contrast to titanium, niobium only slightly improved the transpassive characteristics by lowering the current density for the transpassive breakaway; it did not change the breakdown potential of the base Fe-Cr-V alloy.

The literature does not contain much information on the effect of titanium and niobium on the passive characteristics of stainless steels. A comparison of the polarization curves for Types 304 and 321 alloys in H_2SO_4 shows that titanium is slightly detrimental in causing a few dips in the passive region (Payer and Staehle, 1975). Titanium and niobium are present in precipitates and not in solid-solution so that they are not expected to promote passivation; on the contrary, precipitates are likely sites for initiating corrosion. Titanium is a stronger carbide and nitride former than vanadium and the effect of titanium in raising the breakdown potential indicates that it is forming more stable precipitates than vanadium. Thus, dissolution of a vanadium precipitate may be the reason for the drop in the break-down potential in the Fe-Cr-V alloy.

Nickel. This element has a particularly beneficial effect on the passive characteristics of the Fe-Cr-V-Ti alloys. The most important effects of a 1% nickel addition are a lowering of the critical current density and the minimum current density in the passive region, and a broadening of the passive potential range (Figure 6.19). The beneficial effects of nickel are more apparent at the higher vanadium level: at the 1 and 2.6% vanadium levels nickel actually lowers the breakdown potential. The alloys containing nickel sometimes show up to two dips in the upper half of the passive region (Figure 6.19).

Increasing the nickel content from 1 to 2% improved the passive characteristics of the alloys even further, particularly in lowering the critical current density for primary passivation.

Nickel is well known for the effect it has in improving the passive characteristics of stainless steels in H_2SO_4 and other acids (data summarized by Snape, 1977), and the results here confirm this trend.

Molybdenum, Silicon and Copper. The addition of 1% molybdenum improved

the passivity of the 18Cr-4V-Ti alloy by lowering the critical current
density and the minimum current density in the passive region, and
broadening the passive range, particularly in the breakdown region.
Compared to the Type 444 alloy (Figure 6.20), the 4V-1Mo-Ti alloy
produced a better effect in the lower portion of the passive region
which may indicate some synergistic effect between molybdenum and
vanadium. Although the main reason for adding molybdenum to stainless
steels is to improve the pitting resistance, a subsidiary benefit is in
improved resistance to reducing acids.

Silicon at the 1% level had very little effect on the passivation of
an 18Cr-4V-1.5Ni alloy, the critical current density and passivation
potential being lowered slight'y and the current density in the
passive range being increased somewhat (Figure 6.21). Wilde and
Armijo (1968) also found that silicon (up to 4.2%) had little effect on
the active and passive regions of a 14Cr-14Ni alloy in 1N H_2SO_4, but
they did note that silicon was detrimental in the transpassive region
where it raised the current density for the transpassive transition
(Eta, Figure 6.22). Lizlovs (1966) found a synergistic effect between
molybdenum and silicon in improving the stability of the passive film
in a 17% chromium alloy.

Copper had a generally beneficial effect on the passivity of the
18Cr-4V-1.5Ni base alloy, particularly in reducing the critical current
density, but its effect depended largely on whether or not cathodic
activation was carried out prior to anodic polarization. The curve for
the copper-bearing a⎽⎽⎽, in Figure 6.21 was obtained on a sample which
was cathodically activated. The large anodic peak in the region of
zero potential, as well as the smaller one at about -300 mV, were not
found when the alloy was not cathodically activated. This result
confirms the hydrogen oxidation explanation put forward by Rockel
(1971) to account for the presence of secondary anodic peaks in
anodic polarization curves. Other effects of not cathodically
polarizing were a raising of the free-corrosion and breakdown
potentials.

6.3.2.   Pitting Resistance.   The pitting resistance of the alloys,

determined both potentiodynamically in 0.1N NaCl and by weight loss in
$FeCl_3$, are shown by the results in Table 6.6 (Table 6.7 summarizes the
results). In order to provide some measure of variability of the
pitting potentials, the overall percentage deviation from the mean
is recorded for each of the test temperatures   (Table 6.6). Trends
in the results are interpreted in terms of the actual values recorded
for each alloy, but a finer assessment must consider the precentage
deviations.

Pitting Potential.   A plot of the pitting potentials in Figure 6.23
shows that an increase in vanadium has a beneficial effect on the
pitting potential (and hence resistance to pitting) in all the Fe-Cr-V
alloys. As expected, the pitting potential decreases with an increase
in temperature. The effect found for vanadium confirms the results
of Tomashov et al. (1964) and Climax Molybdenum (unpublished data).
Biefer (1970) found that vanadium at the 1.13% level decreased the
pitting potential in 1N H_2SO_4 + 0.5N NaCl, but increased the value
considerably when the vanadium level was raised to 2.18%. Aslund
(1977) also reported that a 1.1% vanadium level gave a very low
pitting potential in an 18Cr-2.4Mo alloy. An alloy without vanadium
was not examined in this study so that it is not possible to say
whether small additions of vanadium are detrimental as found by
Biefer and Aslund. There is a suggestion in the results of Tomashov
et al. (Figures 4.3 and 4.4 here) that small additions of vanadium
(up to 1.5%) are not as effective as higher additions.

Stabilization of the alloys with titanium and niobium proved detri-
mental at the lowest test temperature (31°C) but was beneficial at
the higher temperatures. The effect of titanium on the pitting
potentials of stainless steels is poorly recorded in the literature
with some studies showing it to be detrimental (Table 4.8) while others
note beneficial effects (Figure 4.4: Aslund, 1977 - synergistic effect
between vanadium and titanium). The results here indicate that
titanium may produce its most beneficial effect at above ambient
temperatures. Stabilization with niobium was found to produce higher
pitting potentials when compared to titanium.

Table 6.6. Pitting Resistance of the Experimental Alloys
Compared to Other Stainless Steels.

Alloy	Pitting Potentials in 0.1N NaCl (mV)[a]			Weight Loss (mdd)[b]
	31°C	59°C	81°C	
1V	200	71	20	1764
1V-Ti	129	105	36	1824
1V-Ti-1Ni	85	96	76	1965
2.6V	285	87	52	2607
2.6V-Ti	193	155	83	670
2.6V-Ti-1Ni	157	183	120	2133
4V	504	192		1942
4V-Nb	442	254		620
4V-Ti	327	227	170	135
4V-Ti-1Ni	341	230	19?	665
4V-Ti-1.5Ni	408	216	163	390
4V-Ti-2Ni	279	224	154	316
4V-Ti-1.5N-Si	464	230	144	42.9
4V-Ti-1.5Ni-Cu	292	228	176	1381
4V-Ti-Mo	595	335	272	2.3
Type 430	~58	-190	-320	4528
Type 316	54	-100	-77	97[c]
Type 444	430	-	-	1250[c]

[a] mV versus SCE

[b] Weight loss in 10% FeCl$_3$, 6H$_2$O at 23°C

[c] From Steigerwald (1974)

Statistics: Percentage deviation from the mean for the pitting
potential at 31°C was $\pm$ 10%; at 59°C, $\pm$ 14%; at 81°C,
$\pm$ 20%

Table 6.7.   Summary of the Effect of Various Alloying Elements
             on the Pitting Resistance of the Experimental
             Alloys

Alloying Element	Pitting Potentials			FeCl$_3$ Weight Loss
	31°C	59°C	81°C	
Vanadium	+	+	+	−
Titanium	−	+	+	+
Niobium	−	+	+	+
Nickel (variable vanadium)	−	+	+	−
Nickel (constant vanadium)	V	V	+	+
Silicon	+	+	−	+
Copper	+	+	+	+
Molybdenum	−	+	+	−

+ = beneficial effect;   − = detrimental effect;

V = variable effect.
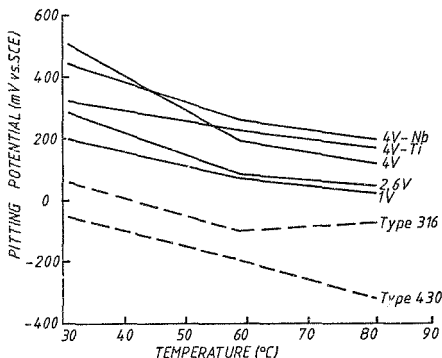
Figure 6.23. The effect of temperature on the pitting potential
           of various experimental alloys compared to Types 316
           and 430 stainless steel.

Regarding the effect of other elements, molybdenum was very beneficial
at all the test temperatures, nickel produced a variable effect, copper
was beneficial only at the higher temperatures (59 and 81°C), and
silicon was detrimental at 81°C. A 1% molybdenum addition to the
4V-Ti alloy raised the pitting potential by 268 mV. This increase
is much greater than the 50 to 100 mV increase found for a 1%
molybdenum addition to a titanium-free 18% chromium alloy with variable
carbon levels (20 to 50 ppm, Lizlovs and Bond, 1975; 300 ppm, Bond,
1973) even considering the 1N NaCl solutions in which they were
tested, and suggests a synergistic interaction between molybdenum,
vanadium and titanium. Aslund (1977) reported a similar effect in
that 0.1% vanadium added to an 18Cr-2.4Mo-Ti alloy raised the pitting
potential by 125 mV in 0.5N NaCl.

The addition of 1% nickel to an Fe-Cr-V-Ti alloy was detrimental at

31°C but beneficial at 59 and 81°C. Increasing the nickel level
from 1 to 2% in a 4V-Ti alloy had a variable effect on the pitting
potential. Horvath and Uhlig(1968) found that nickel increased the
pitting potential of a 15% chromium stainless steel in 0.1N NaCl at
25°C, and Bond (1973) reported that an 18Cr-14Ni-2Mo alloy had a
higher pitting potential than a 17Cr-2Mo alloy in NaCl at 25°C,
except at temperatures above 40°C. The effect of nickel on the pitting
potential of stainless steels therefore appears to depend to some extent
on the presence of other alloying elements,and the same conclusion
probably applies in this study.

The effect of copper on the pitting potential is not well documented.
Copper was found to be quite detrimental at 31°C but was beneficial
at the higher temperatures. This feature,which was also found for
titanium and nickel, may indicate some interaction with other elements.

Silicon is considered to have a beneficial effect on the pitting
resistance of stainless steels and while this is the case for the
lowest temperature studied, 1.5% silicon appeared detrimental at the
higher temperatures. A higher level of silicon is probably needed to
obtain a consistent effect in stainless steels but this can lead to
processing and embrittlement problems.

Examination of the surface of the potentiostat specimens after
deliberate, accelerated pitting showed clearly that precipitates and
surface defects (e.g. polishing scratches, Figure 6.24) were the main
sites for the initiation of pitting. Despite the apparent cleanliness
of the experimental alloys, some large non-metallic precipitates were
found in the pits (Figure 6.25). X-ray analysis of 26 precipitates
revealed the presence of silicon, chromium, vanadium and aluminium
with each element being counted 12 times (Figures 6.26 and 6.27).
Chromium and vanadium were always noted together. Other elements
detected in the precipitates were calcium, potassium and sulphur.

<u>Pitting in FeCl$_3$</u>. The results obtained from weight loss measurements
in FeCl$_3$ did not always correlate with the pitting potential trend
(Table 6.7). From Table 6.6 it can be seen that the Fe-Cr-V alloys
showed the greatest weight loss for all the experimental alloys, with
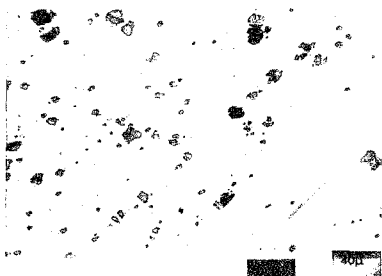
Figure 6.24. Mode of pitting of 18Cr-4V alloy in 0.1N NaCl showing initiation of some pits along polishing scratches.

Figure 6.25. Nature of large elongated precipitate in 18Cr-4V-1i-1.9Ni-1.5Si alloy.

Si   K
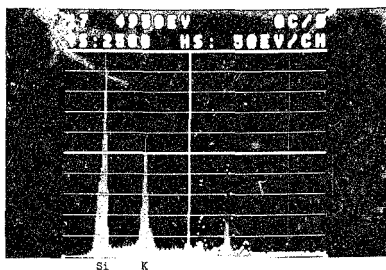
Figure 6.26. EDAX determined composition of precipitate in 18Cr-4V
             alloy around which pitting appears to have been
             initiated. Data represent the base alloy, and the
             grey area the precipitate (Si-K rich).

Al   V Cr Fe
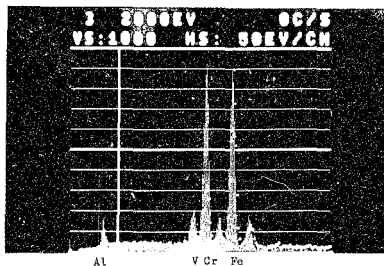
Figure 6.27. EDAX determined composition of precipitate in pit in
             18Cr-4V-Ti alloy. Data represent the base alloy, and
             the grey area the precipitate (Cr-V-Al rich).

increase , vanadium generally being detrimental (Figure 6.28). In contrast, the 4V alloy produced the second highest pitting potential in this study. Both Tomashov et al. (1964) and Biefer (1970) showed that vanadium produced a low weight loss in $FeCl_3$ and that increasing vanadium (above 1.5% in the results of Tomashov et al.) decreased the weight loss. Biefer found that vanadium reduced the weight loss compared to the base alloy, Type 430. (The experimental Fe-Cr-V alloy in this study showed less weight loss than type 430).

Stabilization of the Fe-Cr-V alloys with titanium was beneficial at the 2.6%, and particularly 4%, vanadium level and produced a better result than niobium (Figure 6.29). Titanium has been shown to be detrimental to pitting corrosion in $FeCl_3$ (Moskowitz et al., 1967; Figure 4.3) and the result here may indicate some synergistic effect between vanadium and titanium as was noted in discussing the pitting potentials.

The addition of 1% nickel to the Fe-Cr-V-Ti alloys had a detrimental effect, although only slightly so at the 1% vanadium level (Figure 6.30). Increasing the nickel level from 1 to 2% clearly decreased the weight loss in the alloys. As discussed earlier, the effect of nickel in stainless steels is variable and depends on the presence of other alloying elements, and the results here indicate that nickel may be beneficial in Fe-Cr-V-Ti alloys above a threshold level of 1%.

The most beneficial elements as regards weight loss in $FeCl_3$ were silicon and molybdenum, and these results correlate well with the trend found for the pitting potentials (Figure 6.31). The very low weight loss for the molybdenum -containing alloy compared to Type 444 provides some confirmation of a synergistic effect between molybdenum, vanadium and titanium, referred to earlier in discussing the pitting potentials.

Copper was found to have a detrimental effect in that a 1% addition lead to a more than threefold increase in the weight loss of the base, 4V-Ti-1.5Ni, alloy.

An overall assessment of the effec of alloying on the pitting

Figure 6.29. Results of pitting test in FeCl₃ at 23°C, showing the effect of stabilization with titanium and niobium. Alloys are: 33 = 4V; 37 = 4V-Ti; 34 = 4V-Nb; 40 = 4V-Ti-Ni.
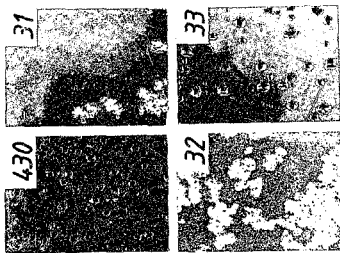
Figure 6.28. Results of pitting test in FeCl₃ at 23°C, showing the effect of vanadium. Alloys are: Type 430; 31 = 1V; 32 = 2.6V; 33 = 4V. Note the different type of pitting in the high vanadium alloy.

Results of pitting test in $FeCl_3$ at 23°C,
showing the effect of vanadium. Alloys
are: type 430; 31 = 1V; 32 = 2.6V;
33 = 4V. Note the different type of
pitting in the high vanadium alloy.
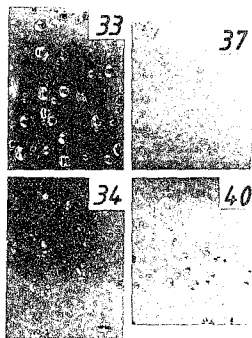
Figure 6.29. Results of pitting test in $FeCl_3$, at 23°C,
showing the effect of stabilization with
titanium and niobium. Alloys are: 33 = 4V;
37 = 4V-Ti; 34 = 4V-Nb; 40 = 4V-Ti-Nb.

Figure 6.31. Results of pitting test in FeCl₃, at 23°C, showing the effect of silicon, copper and molybdenum. Alloys are: 37 = 4V-Ti; 76 = 4V-Ti-1.5Ni-Si; 79 = 4V-Ti-1.5Ni-1Cu; 78 = 4V-Ti-1Mo.

Figure 6.30 Results of pitting test in FeCl₃, at 23°C, showing the effect of nickel. Alloys are: Type 430; 31 = 1V; 35 = 1V-Ti; 38 = 1V-Ti-1Ni.

Figure 6.30 Results of pitting test in FeCl$_3$, at 23°C, showing the effect of nickel. Alloys are: Type 430; 31 = 1V; 35 = 1V-Ti; 38 = 1V-Ti-1Ni.
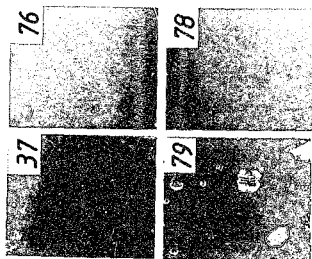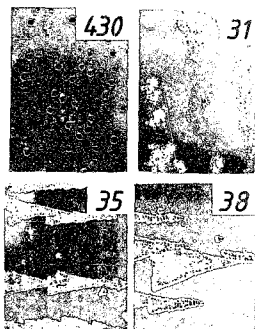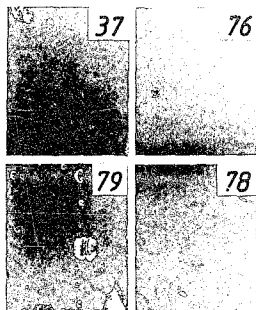

Figure 6.31. Results of pitting test in FeCl$_3$, at 23°C, showing the effect of silicon, copper and molybdenum. Alloys are: 37 = 4V-Ti; 76 = 4V-Ti-1.5Ni-Si; 79 = 4V-Ti-1.5Ni-1Cu; 78 = 4V-Ti-1Mo.

resistance of the experimental alloys must consider the relative merits
of pitting potentials versus weight loss in $FeCl_3$. Since some doubt
still surrounds the use of pitting potentials in practice (although
they usually correlate positively with pitting resistance), the $FeCl_3$
weight loss test must be regarded as more absolute. Vanadium must
therefore be considered as having a variable to somewhat detrimental
effect on pitting corrosion in the 18% chromium alloys studied. The
most promising alloy combinations in this study were 4V-Ti-Mo,.
4V-Ti-Si and 4V-Ti. An important result is the suggestion of a
synergistic effect between molybdenum, vanadium and titanium or
between vanadium and titanium.

6.3.3.   General Corrosion.   The corrosion rates for the alloys in
HNO_3, oxalic and H_2SO_4 acids are presented in Table 6.8.

HNO_3. The 1V and 2.6V alloys showed the highest corrosion rates in
boiling 65% HNO_3, while the 4V alloy had one of the lowest corrosion
rates. Stabilization with titanium was very beneficial at the 1 and
2.6% vanadium levels,but slightly detrimental (as was niobium) in
the 4V alloy. The addition of 1% nickel to the alloys had a
detrimental effect as did silicon, copper and molybdenum, and
increasing nickel from 1 to 2% had a variable effect. The corrosion
rates shown by the experimental alloys are greater than found for the
austenitic and Type 444 stainless steels.

Vanadium appears to have a detrimental effect in HNO_3 at a concentra-
tion below some level between 2.6 and 4%, which may be related to
intergranular corrosion. The fact that the addition of titanium
considerably reduced the corrosion rate indicates that titanium is
removing carbon from some other detrimental precipitate to form a
more corrosion resistant precipitate.

Oxalic Acid. Vanadium had a detrimental effect on the corrosion rate
in boiling 3% oxalic acid, particularly at the 2.6 and 4% levels.
Stabilization with titanium and niobium had a beneficial effect as
did the addition of 1% nickel to a V-Ti alloy. Increasing nickel
from 1 to 2% was beneficial as was the addition of 1.5% silicon to the
base 4V-Ti-1.5Ni alloy, producing the lowest corrosion rate found,

Table 6.8. Corrosion Rates for the Experimental Alloys in HNO₃. Oxalic and H₂SO₄ Acids Compared to Other Stainless Steels.

Table 6.8. Corrosion Rates for the Experimental Alloys in HNO_3, Oxalic and H_2SO_4 Acids Compared to Other Stainless Steels.

Alloy	Corrosion Rate (mpy)			Immersion Period(days)	
	65% HNO_3[a]	3% Oxalic[b]	1N H_2SO_4[c]	HNO_3	Oxalic
1V	144	769	4302	9	2
1V-Ti	19	791	4664	9	5.21
1V-Ti-1Ni	22	509	816	10	6
2.6V	292	3232	3914	10	1.25
2.6V-Ti	25	856	4043	9	5.21
2.6V-Ti-1Ni	40	54	774	11	16
4V	25	3031	2780	9	1.25
4V-Nb	113	741	3043	11	5.21
4V-Ti	34	866	3786	11	5.21
4V-Ti-1Ni	83	54	688	10	16
4V-Ti-1.5Ni	99	30	553	10	16
4V-Ti-2Ni	26	30	632	10	16
4V-Ti-1.5Ni-Si	121	20	907	10	13
4V-Ti-1.5Ni-Cu	120	70	50	10	8
4V-Ti-Mo	126	36	429	10	10
Type 430	28	1147	2267	11	2
Type 304[d]	8	110	–	–	–
Type 316[d]	11	57	15[e]	–	–
Type 444	18	57	422[e]	–	–

[a] Boiling solution

[b] Boiling solution. Active/passive behaviour exhibited by all alloys except V-Si and Types 304 and 316 alloys.

[c] Linear polarization result, at 31°C. Anodic and cathodic Tafel slopes of 80 and 110 m V/decade respectively, assumed

[d] Results from Climax Molybdenum publication on Type 444 alloy.

[e] Results from this study. Type 444 alloy was emery-polished, cold-rolled sheet.

20 mpy. Molybdenum was particularly beneficial, but copper was somewhat detrimental.

The corrosion rates found for the experimental alloys containing nickel (except the 1V-Ti-1Ni alloy) were lower than for the austenitic and Type 444 alloys, a fact which can be ascribed solely to the nickel addition.

As indicated in Table 6.8, most of the alloys showed active/passive behaviour, a feature which is also shown by the Type 444 alloy. All the alloys were covered by a greenish-yellow crust after immersion testing which was shown by X-ray analysis to be hydrated iron oxalate ($FeC_2O_4.2H_2O$).

H_2SO_4. Ferritic stainless steels in general do not have good resistance to H_2SO_4 and this is confirmed by the high corrosion rates found for the experimental alloys. Vanadium appeared to have a detrimental effect but increasing vanadium lowered the corrosion rate slightly (this correlates with the current density data); stabilization with titanium and niobium proved detrimental; nickel was particularly beneficial at all levels; and copper and molybdenum were beneficial with the copper alloy (4V-Ti-1.5Ni-1Cu) showing the lowest corrosion rate (50 mpy). These trends correlate fairly well with the effect of alloying on the passivation of the alloys in H_2SO_4.

In an assessment of the overall effect of alloying on corrosion in the three acids, vanadium appears to have a variable effect in the Cr-V alloy (4% vanadium was particularly beneficial in HNO_3). Stabilization with titanium was beneficial in HNO_3 and oxalic acid, but detrimental in H_2SO_4. The most favourable general alloy combination in terms of resistance to all three acids was V-Ti-Ni, with the addition of copper and silicon (and molybdenum) improving corrosion resistance even further in specific environments. Overall, the best alloy composition was 4V-Ti-1.5Ni-1Cu.

6.3.4. __Intergranular Corrosion.__ Intergranular corrosion was not detected in the alloys in the modified Strauss test ($Cu-CuSO_4-H_2SO_4$)

in either the annealed (825-850°C, water quenched) or sensitized
(1150°C, water quenched) condition. No cracking was observed at
the apexes of the bend at a magnification of 30X in the vanadium-
bearing specimens bent through 170°C, but the sensitized Type 430
alloy broke in half on being bent. It can be concluded that none
of the alloying elements induce susceptibility to intergranular
corrosion and that significant chromium carbide precipitation
does not occur at the grain boundaries.

Intergranular corrosion can be prevented in 18% chromium stainless
steels by lowering the combined carbon and nitrogen level to
below 100-80 ppm (Table 2.2) (Demo and Bond, 1975), or stabilizing
with elements such as titanium and niobium, or having high vanadium
levels. The combined carbon and nitrogen level of the Cr-V alloys
varied from 94 to 157, which is on the borderline of susceptibility
to intergranular corrosion. Climax Molybdenum found that inter-
granular corrosion occurred in 18Cr-V stainless steels with a
combined carbon and nitrogen level of 300 ppm, when the vanadium
level was decreased from 3 to 2% (Table 4.3).

7. SUMMARY

10.1.   Tensile Properties.   The addition of up to 4% vanadium to an
18% chromium ferritic stainless steel containing a combined carbon and
nitrogen content in the range 94 to 117 ppm had a variable effect on
the tensile properties: relative to the 18Cr-1V alloy, the tensile
and ultimate strength values were greater in the 4V alloy but lower in
the 2.6V alloy.   Increasing vanadium generally decreased the ductility
of the alloys.

Stabilization of the 18Cr-V alloy with 0.1% titanium reduced the
strength and had a variable effect on the ductility.   Niobium had a more
beneficial effect than titanium.   The addition of up to 2% nickel to an
18Cr-V-Ti alloy raised the strength and generally improved the ductility.
The separate addition of from 1 to 1.5% of silicon, copper and
molybdenum to an 18Cr-V-Ti alloy (with 1.5% nickel in the case of the
silicon and copper alloys) raised the strength, particularly in the
case of silicon.

The effect of alloying on the tensile properties of an 18Cr stainless
steel is interpreted largely in terms of precipitation phenomena;   the
alloys are all single phase ferritic.

10.2.   Toughness.   Vanadium was found to have a very beneficial
effect on the impact (ductile-to-brittle) properties of an 18% chromium
stainless steel.   Full-size Charpy V-notch specimens showed a transition
temperature of 85.5°C for a 1% vanadium addition (measured at 100
Joules), compared to 70.5 and 27°C for 2.6 and 4% vanadium additions
respectively.   Scanning electron microscopy shows very fine
precipitates in all the alloys and the results probably reflect the
tendency for detrimental chromium carbide precipitates to form at low
vanadium levels,thereby reducing the toughness of the alloy, or to some
solid-solution strengthening effect of vanadium.

Stabilization of the 18Cr-V alloy with titanium had the opposite effect
in that the 4V alloy showed the higher transition temperature (92°C)
compared to the 1V alloy (46.5°C).   Niobium only slightly raised the
transition temperature in the 4V alloy (52.5°C).   Considerably larger
size precipitates are present in the titanium-stabilized alloys (but

not in the case of niobium compared to the unstabilized alloys, and
the results can be interpreted in terms of titanium carbonitride pre-
cipitation associated with an increasing vanadium content.

Regarding the effect of other elements in an 18Cr-V-Ti alloy, nickel
was generally beneficial, as was copper. Silicon and molybdenum were
slightly detrimental.

10.3.   Passivity.   The passive characteristics of the 18% chromium
stainless steel in 1N H_2SO_4 was found to be little improved by
alloying with vanadium. Although the critical current density and
potential for primary passivation were lowered, vanadium reduced the
breakdown potential due to incipient breakaway of the transpassive
potential.

The most significant effect of stabilization with titanium was to
raise the breakdown potential in the 18Cr-V alloy, thus eliminating
early breakaway of the transpassive region. Titanium and vanadium
appeared to combine synergistically. Stabilization with niobium only
slightly raised the breakdown potential.

Nickel had a particularly beneficial effect on the passive characteristics
of the 18Cr-V-Ti alloy, the most notable effects being a lowering of
the critical current density and the minimum current density in the
passive region, and a broadening of the passive potential range.
Adding 1% molybdenum to an 18Cr-4V-Ti alloy considerably improved the
passive characteristics and there was an indication of a synergistic
effect between molybdenum and vanadium. Silicon had little effect on
the passivation characteristics, but copper was very beneficial when
cathodic activation was not performed prior to anodic polarization.
The 18Cr-4V-Ti-1.5Ni-1Cu alloy showed a very low critical current
density value.

10.4.   Pitting.   Published data on the effect of vanadium in stainless
steels emphasize the beneficial effect of vanadium in reducing pitting
corrosion. While vanadium, in this study, increased the pitting
potential of the 18% chromium alloy in 0.1N NaCl, it had a variable
to detrimental effect in an assessment of pitting in a $FeCl_3$ solution.

On balance, therefore, vanadium must be regarded as variable in its
effect on the pitting resistance of low-interstitial 18% chromium
stainless steels.

Stabilization with titanium and niobium had a variable effect on the
pitting potential and the weight loss tests in $FeCl_3$. However, in
both tests the 18Cr-4V-Ti alloy showed increased resistance to pitting
relative to the 18Cr-IV-Ti alloy. The results may indicate a
synergistic effect between vanadium and titanium.

Regarding the effect of other alloying elements, molybdenum was very
beneficial (as expected), as was silicon, while nickel and copper had
variable effects. To summarize, the most promising alloy combinations
as regards pitting were: 4V-Ti-Mo, 4V-Ti-Si and 4V-Ti.

10.5.   General Corrosion.   In an assessment of the overall effect of
alloying on corrosion in concentrated HNO_3, 3% oxalic acid and 1N
H_2SO_4, vanadium appears to have a variable effect in the 18Cr-V stainless
steels (4% vanadium was particularly beneficial in HNO_3). Stabilization
with titanium was beneficial in HNO_3 and oxalic acid, but detrimental re-
in H_2SO_4. The most favourable general alloy combination in terms of re-
sistance to all three acids was Cr-V-Ti-Ni, with the addition of copper
and silicon(and molybdenum) improving corrosion resistance even further
in specific acids. Overall, the best alloy composition was
18Cr-4V-Ti-1.5Ni-1Cu.

10.6.   Intergranular Corrosion Resistance.   Testing of both sensitized
(1150°C) and annealed (850°C) alloys showed that neither vanadium nor
any of the other alloying elements lead to intergranular corrosion in
the modified Strauss test. The experimental alloys have very low
interstitial element levels and this is the main reason they are
resistant to this form of corrosion.

10.7.   Future Research.   The most important result to come out of this
study has been the effect of vanadium in improving the toughness of
the 18% chromium ferritic stainless steel. The way in which vanadium
acts to improve toughness, however, remains unanswered, and future
research should concentrate firstly on solving this problem and thus

providing some quantitative basis for the choice of future alloying
combinations.

Unfortunately, the alloy combinations showing the best toughness,
4V, 4V-Nb and 1V-Ti-Ni have their limitations as regards corrosion
resistance. Since poor toughness is the main drawback to the more
general use of ferritic stainless steels, future research should
examine alloying combinations from the point of view of good corrosion
resistance while at the same time retaining the improved toughness
conferred by the vanadium addition. Nickel and molybdenum were found
to be the most favourable elements as regards corrosion resistance, and
alloying combinations that may show promise in 18% chromium ferritic
stainless steels from the viewpoints of toughness and corrosion
resistance are V-Ni-Mo or V-Ni-Nb-Mo. Stabilization with titanium works
against an increasing vanadium content in improving toughness, but the
1V-Ti-Ni-Mo combination may be a promising line for research. This
study has shown some indication of a synergistic effect between
vanadium and titanium (and molybdenum) and future research should aim
to clarify this point.

The present study has examined alloys with a low interstitial element
level varying within fairly narrow limits. Future research should
therefore consider the effect of vanadium at various interstitial
levels. Above a concentration of 3%, vanadium may act as a stabilizer
in the same way as titanium and niobium do in small amounts.

One important aspect to consider is the effect of the vanadium and
nickel combination on the susceptibility of ferritic stainless steel
to stress-corrosion cracking. A particular advantage of the present
commercially available ferritic stainless steels is their resistance
to stress-corrosion cracking, and future vanadium-bearing derivatives
of these alloys should therefore also retain this property. The
necessity to retain resistance to cracking may limit the full advantage
to be gained from the nickel addition.

Precipitates (and solid-solution effects in some cases) play a major
role in determining the mechanical and corrosion properties of stainless
steels. It is essential therefore that detailed optical and scanning

transmission electron microscopy be carried out in conjunction with
the research suggested above. Lack of such data is one of the
limitations on conclusions that have been drawn in the present thesis.

8. ACKNOWLEDGEMENTS

9. REFERENCES

ABO, H., NAKAZAWA, S., TAKAMURA, S., ONOYAMA, M., OGAWA, H and OKADA, H.
    The role of carbon and nitrogen on the toughness and inter-
    granular corrosion of ferritic stainless steels. In "Stainless
    Steel '77", Climax Molybdenum Symposium, London, 1977, p.35.

AGARWALA, V.S. and BIEFER, G.J. Corrosion of Type 430 stainless steel:
    effects of Mo-Pd and other addition pairs. Corrosion,
    Vol.28, p.65 (1972).

ARGENT, B.B., VAN NIEKERK, M.N. and REDFERN, G.A. Creep of ferritic
    steels. J.I.S.I., Vol.208, p.830 (1970).

ARNESS, W.B. Rustless iron. U.S. Patent No. 2310341, February 9, 1943.

ASLUND, C. Properties and applications of low interstitial 18 and
    25% Cr-Mo ferritic stainless steels. In "Stainless Steel '77",
    Climax Molybdenum Symposium, London, 1977, p.173.

BAERLECKEN, E., FISCHER, W.A. and LORENZ, K. Studies of transformation
    behaviour, the notch impact toughness and the tendency toward
    intercrystalline corrosion in iron-chromium alloys, with
    chromium contents up to 30%. Stahl und Eisen, Vol.81, p.768
    (1961).

BERAHA, E. New metallographic reagents for stainless steel and heat-
    resisting alloys. J.I.S.I., Vol.204, p.248 (1966).

BIEBER, C.G. High-chromium steel resistant to pitting and crevice
    corrosion. U.S. Patent No. 3895940, July 22, 1975.

BIEFER, G.J. Effects of alloying on polarization and corrosion of
    Type 430 stainless steel. Canadian Met. Quart., Vol.9,
    p.537 (1970).

BINDER, W.O. and SPENDELOW, H.R. The influence of chromium on the
    mechanical properties of plain chromium steels. Trans. ASM,
    Vol. 43, p.759 (1951).

BINDER, W.O. "Corrosion of Metals". American Soc. Metals, 1965, p.56.

BOND, A.P. and DUNDAS, H.J. Effects of composition on the stress-
    corrosion cracking of ferritic stainless steels. Corrosion,
    Vol.24, p.344 (1968).

BOND, A.P. and LIZLOVS, E.A. Intergranular corrosion of ferritic
    stainless steels. J. Electrochem. Soc., Vol. 116, p. 1305
    (1969).

BOND, A.P. Effects of molybdenum on the pitting potentials of ferritic
    stainless steels at various temperatures. J. Electrochem.
    Soc., Vol.120, p.603 (1973).

BOND, A.P. and DUNDAS, H.J. (1973) Unpublished data. Climax Molybdenum
        Co., Reported in Steigerwald et al. (1977).

BOND, A.P., DUNDAS, H.J. LIZLOVS, E.A., GEMMEL, E.A. and SOLLY, B.
        Corrosion resistance and mechanical properties of nickel-bearing
        ferritic stainless steels. Werkstoffe und Korr., Vol.28,
        p.536 (1977).

BORGGREEN, K. and THOLEN, A.R. Creep mechanisms in a vanadium alloyed
        austenitic stainless steel. Met. Trans., Vol. 7A, p.1615 (1976).

BRANDIS, H., KIESHEYER, H., KUPPERS, W. and OPPENHEIM, R. Dew Technische
        Berichte, Vol.2, p.3 (1976). Reported in Steigerwald et al.
        (1977).

BRIGHAM, R.J. and TOZER, E.W. Effect of alloying additions on the
        pitting resistance of 18% Cr austenitic stainless steel.
        Corrosion, Vol.30, p.161 (1974).

C.

CHERNOVA, G.D. and TOMASHOV, N.D. Corros. Met. Alloys, No.5, p.1 (1965).
        Reported in Snape (1977).

CIGADA, A., SINIGAGLIA, C and BORILE, F. Contribution to the
        interpretation of current maxima in the passivity range of
        austenitic stainless steels. Corrosion, Vol.34, p.407 (1978).

COOKE, C.H. (1950). Reported in E.O. Hall and S.H. Algie, The sigma
        phase, Met. Reviews, Vol.11, p.61 (1966).

COPSON, H.R. In "Physical Metallurgy of Stress-Corrosion Fracture",
        Rhodin, T.N. (Editor), Interscience, 1959.

D.

DA CUNHA BELO, M., RONDOT, B., PONS, F., LE HERICY, J. and LANGERON, J.P.
        Study by Auger spectrometry and cathodic reduction of passive
        films formed on ferritic stainless sterls. J. Electrochem.
        Soc., Vol.124, p.1317 (1977).

DAVIS, J.E., DEVERELL, H.E. and NICHOL, T.J. Intergranular corrosion
        resistance of a 26Cr-1Mo ferritic stainless steel containing
        niobium. Corrosion, Vol.36, p.215 (1980).

DEFILIPPI, J.D. and RATZ, G.A. Vanadium-stabilized martensitic
        stainless steel. U.S. Patent No. 3933479, January 20, 1976.

DELNICK, F.M. and HACKERMAN, N. Passive iron: a semi-conductor model
        for the oxide film. J. Electrochem. Soc., Vol.126, p.732
        (1979)

DEMO, J.J. Weldable and corrosion-resistant ferritic stainless steel.
        Met. Trans., Vol.5, p.2253 (1974).

DEMO, J.J. and BOND, A.P. Intergranular corrosion and embritttlement of ferritic stainless steels. Corrosion, Vol.31, p.21 (1975).

DEMO, J.J. Structure and constitution of wrought ferritic stainless steels. In "Handbook of Stainless Steels", D. Peckner and I.M. Bernstein (Editors), McGraw-Hill, 1977, p.5-1.

DESESTRET, A. and WAGNER, G.H. Erweiterte Diskussions - bemerkungen zum Einfluss von Silicum und Molybdän auf die Spannungsriss-kortosions empfindlichkeit austeintscher und austenoferritischer Chrom-Nickel-Stähle. Werk.und Korr., Vol.20, p.300 (1969).

DIJKSTRA, L.J. and SLADEK, R.J. Effect of alloying elements on the behaviour of nitrogen in alpha iron. Trans-AIME, Vol. 197, p.69 (1953).

DUNDAS, H.J. Unpublished data, Climax Molybdenum Co..Reported in Steigerwald et al. (1977), p.59.

F.

FLOREEN, S. and HAYDEN, H.W. The influence of austenite and ferrite on the mechanical properties of two-phase stainless steels having microduplex structures. Trans. ASM, Vol.61, p.489 (1968).

FLOREEN, S. "Chromium Substitution in Stainless Steels." Report No. Bu Mines OFR 110-81, Bureau of Mines, U.S. Dept. of Interior, 1980.

FRANCE, W.D. and GREENE, N.D. Interpretation of passive current maxima during polarization of stainless steels. Corrosion, Vol.24, p.403 (1968).

FRANKENTHAL, R.P. On the passivity of iron-chromium alloys. Part III - Effect of potential. J. Electrochem. Soc., Vol.116, p.1646 (1969).

G.

GATES, J.D. and JAGO, R.A. "Breakdown of Stabilization in Type 444 Ferritic Stainless Steel". Proceedings, 35th Annual Conference of the Australasian Institute of Metals, Sydney, p.82 (1982).

GREENE, N.D. Predicting the behaviour of corrosion resistant alloys by potentiostatic polarization methods. Corrosion, Vol.18, p.136t (1962).

GROBNER, P.J. The 885°F (475°C)ombrittlement of ferritic stainless steels. Met. Trans., Vol.4, p.251 (1973).

GRUBB, J.F. and WRIGHT, R.N. The role of C and N in the brittle fracture of Fe-26Cr. Met. Trans. A. Vol. 10A, p.1247 (1979).

H.

HANNINEN, H.E. Influence of metallurgical variables on environment-sensitive cracking of austenitic alloys. Int. Metals Rev., Vol.24, p.85 (1979).

HEGER, J.J. 885°F embrittlement of ferritic chromium-iron alloys.
        Metal Progress, Vol.60, p.55 (1951).

HORVATH, J. and UHLIG, H.H. Critical potentials for pitting corrosion
        of Ni, Cr-Ni, Cr-Fe, and related stainless steels. J.
        Electrochem.Soc., Vol.115, p.791 (1968).

HOUDREMONT, E. and TOFAUTE, W. Kornzerfalls-Lestandigkeit nichtrostender
        ferritischer und martensitischer Chromstähle. Stahl u Eisen,
        Vol. 72, p.539 (1952).

                                                                    I.

IRANI, J.J. and WEINER, R.T. Aging behaviour of an austenitic steel
        containing vanadium J.I.S.I., Vol.203, p.913 (1965).

IRVINE, K.J. LLEWELLYN, D.T. and PICKERING, F.B. High-strength
        austenitic stainless steel. J.I.S.I., Vol.199, p.153 (1961).

                                                                    K.

KIESLING, R. A new ferritic-austenitic stainless steel for combating
        stress-corrosion cracking. Scand. J. Metallurgy,   Vol.1,
        p.185 (1972).

KOUTANIEMI, P., HEIKKINEN, V. and SAARINEN, A. Effect of vanadium on
        475°C embrittlement of a chromium steel. Metal Sci., Vol.8,
        p.94 (1974).

KRIVOBOK, V.N. Alloys of iron and chromium. Trans. ASM, Vol.23,
        p.1 (1935).

KRUPP, F, A.G. British Patent 2137349,27 October, 1930. The date of
        the corresponding and original German Patent is 26 June, 1929.

                                                                    L.

LANGER, N.A., YAGUPLSKAYA, L.N., KAKHOVSKII, N.I., YUSHCHENKO, K.A.,
FARTUSHNYI, V.G. and CHALYUK, G.I. Corrosion resistance of steels
        with a low concentration of nickel in aggressive media. Metal
        Sci. Heat Treatment, p.121 (1966).

LENA, A.J. Sigma phase - a review. Metal Progress, Vol.66, p.86
        (1954).

LENA, A.J., LULA, R.A. and KIEFER, G.C. Discussion on paper by Nehrenberg
        and Lillys (1954). Trans. ASM, Vol.46, p.1203 (1954).

LENNARTZ, G. and KIESHEYR, H. Korrosion Verhalten von hochchromhaltigen,
        ferritischen Stählen. DEW Technische Berigte, Vol.11, p.230
        (1971).

LIZLOVS, E.A. Effects of Mo, Cu, Si and P on anodic behaviour of 17Cr
        steels. Corrosion, Vol.22, p.297 (1966).

LZILOVS, E.A. and BOND, A.P. Anodic polarization of some ferritic
        stainless steels in chloride media. J. Electrochem. Soc.,
        Vol.116, p.574 (1969).

LIZLOVS, E.A. and BOND, A.P. Anodic polarization of 25% chromium ferritic stainless steels. J. Electrochem. Soc., Vol.118, p.22 (1971).

LIZLOVS, E.A. The effect of 885F (475C) embrittlement on resistance to pitting corrosion of 18Cr-2Mo stainless ..ee' modified with Mn, Co, Ni, Al, V and Si additions.Internal Report, Climax Molybdenum Research Lab., Ann Arbor, Michigan, U.S.A. (1974).

LIZLOVS, E.A. and BOND, A.P. The effect of low-temperature ageing on corrosion resistance of 18Cr-2Mo titanium stabilized ferritic stainless steel. J. Electrochem. Soc., Vol. 122, p.589 (1975).

LIZLOVS, E.A. and BOND, A.P. Anodic polarization behaviour of high-purity 13 and 18% Cr stainless steels. J.Electrochem. Soc., Vol. 122, p.719 (1975).

LULA, R.A., LENA, A.J. and KIEFER, G.C. Intergranular corrosion of ferritic stainless steels. Trans. ASM, Vol.46, p.197 (1954).

LUMSDEN, J.B. and STAEHLE, R.W. Application of Auger election spectro-scopy to the determination of the composition of passive films on type 316SS. Scripta Metallurgica, Vol.6, p.1205 (1972).

M.

MAN, H.C. and GABE, D.R. The determination of pitting potentials. Corr. Science, Vol.21, p.323 (1981).

MARTENS, M. and DUWEZ, P. Phase relationships in the iron-chromium-vanadium system. Trans. ASM, Vol.44, p.484 (1952).

MATSUSHIMA, S. and ISHIHARA, T. Effect of impurities on stress-corrosion cracking of 18Cr ferritic stainless steel. Trans. Nat. Inst. Metals, Japan, Vol.17, p.14 (1975).

McQUEER, J.I. The effect of molybdenum and other alloying elements on the pitting corrosion resistance of stainless steels: a literature survey. National Physical Res. Lab. Report, F15 No.195, CSIR. Pretoria, 1979.

MEDIRATTA, S.R. and RAMASWAMY, V. Physical metallurgy of ferritic stainless steel. Tool and Alloy Steels Annual, p.451 (1976).

MIMA, G., YAMAGUCHI, M. and TAKAHASHI, J. Trans. Japan Inst. Metals, Vol.9, p.407 (1968). Reference from Koutaniemi et al. (1974).

MOODY, J.R. The corrosion of vanadium-containing stainless steels: a literature survey. Unpublished report, Vanadium International Technical Committee, London, 1979.

MOSKOWITZ, A., SALTZMAN, G.A. PINNOW, K.E. and REDMERSKI, L.S. Influence of residual and minor elements on the pitting and atmospheric corrosion resistance of austenitic stainless steels. In "Effects of Residual Elements on Properties of Stainless Steels". ASTM, STP 418, Am.Soc.Testing Mats., 1967, p.3.

N.

NEHRENBERG, A.E. and LILLYS, P. High temperature transformations in
        ferritic stainless steels containing 17 to 25% chromium.
        Trans. ASM, Vol.46, p.1177 (1954).

NEWELL, H.D. Properties and characteristics of 27% chromium-iron.
        Metal Progress, Vol.49, p.977 (1946).

NUNES, J. Influence of test temperature and solute additions on tensile
        properties of α-iron. J.I.S.I., Vol.204, p.371 (1966).

NOVAK, C.J. Structure and constitution of wrought austenitic stainless
        steels. In "Handbook of Stainless Steels", D. Peckner and
        I.M. Bernstein (Editors), McGraw-Hill, 1977, p.4-1.

O.

ODESKII, D.A., VOZDVIZHENSKII, V.M., POSTNOVA, A.D. and LIVANOVA, R.P.
        Effect of vanadium on the ductility of nickel-free ferritic
        stainless steel. Met. Sci. Heat Treatment, Vol.20, p.409 (1978).

OKADA, H., HOSOI, Y. and OGAWA, H. J. Iron and Steel Inst. (Japan),
        Vol.59, p.5155 (1973). Reported in Steigerwald et al. (1977).

OSOZAWA, K., OKATO, N., FUKASE, Y. and YOKOTA, K. Effects of alloying
        elements on the pitting corrosion of stainless steel. Int.
        Corrosion Conf. Ser., NACE, p.270,(1976).

P.

PAYER, J.H. and STAEHLE. R.W. The dissolution behaviour of $Cr_{23}C_6$ and
        TiC related to the stainless steels in which they occur.
        Corrosion, Vol.31, p.30 (1975).

PLUMTREE, A. and GULLBERG, R. The influence of interstitial content on
        the ductile-brittle transition temperature of Fe-25Cr ferritic
        stainless steels. J. Testing and Evaluation, ASTM, Vol.2,
        p.331 (1974).

POLLARD, B. Effect of titanium on the ductility of 26% chromium, low
        interstitial ferritic stainless steel. Metals Tech., Vol.1,
        p.31 (1974).

POULSON, B.S. and PARKINS, R.N. Effect of Ni additions upon the stress
        corrosion of ferritic steels in a chloride environment.
        Corrosion, Vol.29, p.414 (1973).

POURBAIX, M. "Atlas of Electrochemical Equilibria in Aqueous Solutions".
        Pergamon Press, 1966.

R.

RIEDRICH, G and HOCH, G. Effects of vanadium on intercrystalline
        corrosion of austenitic chromium-nickel steels. Stahl und
        Eisen, Vol.55, p.30 (1940).

ROCKEL, M.B. Interpretation of the second anodic current maximum on
        polarization curves of sensitized chromium steels in 1N H_2SO_4.
        Corrosion, Vol.27, p.95 (1971).

ROSTOKER, W. "The Metallurgy of Vanadium". Wiley and Sons, 1958, p.90.

S.

SAGE, A.M. Effect of vanadium, nitrogen and aluminium on the mechanical
        properties of reinforcing bar steels. Metals Tech., Vol.3,
        p.65 (1976).

SANDOMIRSKII, M.M. Effect of copper on the mechanical properties of
        steels of different classes. Metal Sci. Heat Treatment, Vol.20,
        p.414 (1978).

SAWHILL, J.M. and BOND, A.P. Ductility and toughness of stainless steel
        welds. Welding J. (Res. Supplement), Vol.55, p.33s (1976).

SCHICK, K.L. "Thermodynamics of Certain Refractory Compounds".
        Academic Press, New York, 1966.

SCHMIDT, W. and JARLEBORG, O. "Ferritic Stainless Steels with 17% Cr."
        A Climax Molybdenum Co. publication, 1974.

SCURR, W.J. Vanadium additions to 3CR12 type steels. Unpublished
        memo to manager, Metallurgical Services, Middelburg Steel and
        Alloys, September 21, 1978.

SEMCHYSHEN, M.A., BOND, A.P. and DUNDAS, H.J. Effects of composition
        on ductility and toughness of ferritic stainless steel. In
        "Symposium Toward Improved Ductility and Toughness", Climax
        Molybdenum Symposium, Kyoto, Japan, 1971, p.239.

SHATYNSKI, S.R. The thermochemistry of transition metal carbides.
        Oxidation of Metals, Vol.13, p.105 (1979).

SHAW, S.W.K. and QUARRELL, A.G. The formation of carbides in low – carbon
        chromium – vanadium steels at 700°C J.I.S.I., Vol. 185, p.10
        (1957).

SHINODA, T., ISHII, T., TANAKA, R., MININO, T., KINOSHITA, K and
MINEGISHI, I. Effects of some carbide stabilizing elements on creep –
        rupture strength and micro–structural changes of 18-10
        austenitic steel. Vol.4, Met. Trans., p.1213 (1973).

SHORTSLEEVE, F.J. and NICHOLSON, M.E. Transformation in ferritic
        chromium steels between 1100 and 1500°F (595 and 815°C).
        Trans. ASM Vol.43, p.142 (1951).

SILCOCK, J.M. Precipitation in austenitic steels containing vanadium.
        J.I.S.I., Vol.211, p.792 (1973).

SIPOS, D.J., STEIGERWALD, R.F. and WHITCOMB, W.E. Ductile corrosion-
        resistant ferrous alloys containing chromium. U.S. Patent
        No. 3672876, June 27, 1972.

SNAPE, E. Effect of nickel on the structure and properties of wrought
    and cast stainless steels. In "Handbook of Stainless Steels",
    McGraw-Hill, Penkner, D. and Bernstein, I.M., Editors, 1977.

STEIGERWALD, R.F. New molybdenum stainless steels for corrosion
    resistance: a review of recent developments. Materials
    Performance, Vol.13, p.9 (1974).

STEIGERWALD, R.F., DUNDAS, H.J., REDMOND, J.D. and DAVISON, R.M. The
    physical metallurgy of Fe-Cr-Mo ferritic stainless steels. In
    "Stainless Steel '77', Climax Molybdenum Symposium, London,
    1977, p.57

STIMMING, U. and SCHULTZE, J.W. A semi-conductor model of the passive
    layer on iron electrodes and its application to electrochemical
    reactions. Electrochimica Acta, Vol.24, p.859 (1979).

STREICHER, M.A. Pitting corrosion of 18Cr-8Ni stainless steel.
    Corrosion, Vol.103, p.375 (1956).

STREICHER, M.A. Corrosion of stainless steels in boiling acids and its
    suppression by ferric salts. Corrosion, Vol.14, p.59t (1958).

STREICHER, M.A. Development of pitting resistant Fe-Cr-Mo alloys.
    Corrosion, Vol.30, p.77 (1974).

STREICHER, M.A. Stainless Steels : Past, Present and Future. In
    "Stainless Steel '77", Climax Molybdenum Symposium, London,
    1977, p.1.

SZKLARSKA - SMIALOWSKA, Z. Review of literature on pitting corrosion
    published since 1960. Corrosion, Vol.27, p.223 (1971).

7.

TETELMAN, A.S. and McEVILY, A.J. "Fracture of Structural materials."
    Wiley and Sons, 1967, p.509.

THIELSCH, H. Physical and welding metallurgy of chromium stainless
    steels. Welding J. (Res. Supplement), Vol.30, p.209s
    (1951).

THOMPSON, A.W. and BERNSTEIN, I.M. The role of metalurgical variables
    in hydrogen - assisted environmental fracture. In "Advances
    in Corrosion Science and Technology", Vol.7, Fontana and
    Staehle (Editors), 1979, p.53.

THUM, E.E. (Editor). "The Book of Stainless Steels". American Soc.
    Metals, 1935.

TOMASHOV, N.D., CHERNOVA, G.P. and MARCOVA, O.N. Effect of supplementary
    alloying elements on pitting corrosion susceptibility of
    18Cr-14Ni stainless steel. Corrosion, Vol.20, p. 166t (1964).

TRUMAN, J.E. Unpublished data. Brown-Firth Research Laboratories, 1953.

SNAPE, E. Effect of nickel on the structure and properties of wrought
        and cast stainless steels. In "Handbook of Stainless Steels",
        McGraw-Hill, Peckner, D. and Bernstein, I.M., Editors, 1977.

STEIGERWALD, R.F. New molybdenum stainless steels for corrosion
        resistance: a review of recent developments. Materials
        Performance, Vol.13, p.9 (1974).

STEIGERWALD, R.F., DUNDAS, H.J., REDMOND, J.D. and DAVISON, R.M. The
        physical metallurgy of Fe-Cr-Mo ferritic stainless steels. In
        "Stainless Steel '77', Climax Molybdenum Symposium, London,
        1977, p.57

STIMMING, U. and SCHULTZE, J.W. A semi-conductor model of the passive
        layer on iron electrodes and its application to electrochemical
        reactions. Electrochimica Acta, Vol.24, p.859 (1979).

STREICHER, M.A. Pitting corrosion of 18Cr-8Ni stainless steel.
        Corrosion, Vol.103, p.375 (1956).

STREICHER, M.A. Corrosion of stainless steels in boiling acids and its
        suppression by ferric salts. Corrosion, Vol.14, p.59t (1958).

STREICHER, M.A. Development of pitting resistant Fe-Cr-Mo alloys.
        Corrosion, Vol.30, p.77 (1974).

STREICHER, M.A. Stainless Steels : Past, Present and Future. In
        "Stainless Steel '77", Climax Molybdenum Symposium, London,
        1977, p.1.

SZKLARSKA - SMIALOWSKA, Z. Review of literature on pitting corrosion
        published since 1960. Corrosion, Vol.27, p.223 (1971).

                                                                    T.

TETELMAN, A.S. and McEVILY, A.J. "Fracture of Structural materials."
        Wiley and Sons, 1967, p.509.

THIELSCH, H. Physical and welding metallurgy of chromium stainless
        steels. Welding J. (Res. Supplement), Vol.30, p.209s
        (1951).

THOMPSON, A.W. and BERNSTEIN, I.M. The role of metalurgical variables
        in hydrogen - assisted environmental fracture. In "Advances
        in Corrosion Science and Technology", Vol.7, Fontana and
        Staehle (Editors), 1979, p.53.

THUM, E.E. (Editor). "The Book of Stainless Steels". American Soc.
        Metals, 1935.

TOMASHOV, N.D., CHERNOVA, G.P. and MARCOVA, O.N. Effect of supplementary
        alloying elements on pitting corrosion susceptibility of
        18Cr-14Ni stainless steel. Corrosion, Vol.20, p. 166t (1964).

TRUMAN, J.E. Unpublished data. Brown-Firth Research Laboratories, 1953.

TRUMAN, J.E. Corrosion-resisting steels. Metals and Materials, Vol.2,
         p.208 (1968).

TRUMAN, J.E. and PIRT, K.R. Resistance to oxidation at elevated
         temperatures of a number of alloy steels. Br. Corros, J.,
         Vol.11, p.188 (1976).

TRUMAN, J.E. Stainless Steel Ind., Vol.6, p.21 (1978).

TRUMAN, J.E. and PIRT, K.R. Effects of various alloying additions on
         the resistance to oxidation at elevated temperatures of 18%
         chromium austenitic steel. Br. Corros. J., Vol.13, p.136
         (1978).

                                                                  U.

UHLIG, H.H. "Corrosion and Corrosion Control." Wiley and Sons,
         1971, p.90

                                                                  W.

WERT, C. Diffusion and precipitation of carbon in some alloys of iron.
         J. Metals, Trans-AIME, June, p.602 (1952).

WILDE, B.E. and ARMIJO, J.S. Influence of silicon and manganese on
         corrosion behaviour of austenitic stainless steels. Corrosion,
         Vol.24, p.393 (1968).

WILDE, B.E. and GREENE, N.D. The variable corrosion resistance of
         18Cr-8Ni stainless steels : behaviour of commercial alloys.
         Corrosion, Vol.25, p.300 (1969).

WOODHEAD, J.H. and QUARRELL, A.G. "The Role of Carbides in Low-alloy
         Creep-resisting Steels." A Climax Molybdenum Co. Publication,
         1965.

WRIGHT, R.N. Mechanical behaviour and weldability of a high chromium
         ferritic stainless steel as a function of purity. Welding J.
         (Res. Supplement), Vol.50, p.434s (1971).

WYLIE, R.O. Low carbon ferritic stainless steel. U.S. Patent
         No. 3023098, Feb.27, 1962.

WILLIAMS, R.O. Further studies of the iron-chromium system. Trans.
         Metall. Soc. AIME, Vol.212, p.497 (1958).

Additional References

HODGES, R.J. Intergranular corrosion in high-purity ferritic stainless
         steels: isothermal time-temperature sensitization measurement.
         Corrosion, Vol.27, p.164 (1971).

STREICHER, M.A. "Theory and Application of Evaluation Tests for
         Detecting Susceptibility to Intergranular Attack in
         Stainless Steels and Related Alloys - Problems and
         Opportunities". ASTM/STP 656, p.3 (1978).

R.D. DAVIES, Ph.D. and F.P.A. ROBINSON, Ph.D., Department of Metallurgy, University of the
Witwatersrand, Johannesburg, South Africa.
The Effect of Vanadium and Other Elements on the Mechanical and Corrosion Resistant Properties of
Ferritic Stainless Steels.

THE EFFECT OF VANADIUM AND OTHER ELEMENTS ON THE
MECHANICAL AND CORROSION RESISTANT PROPERTIES OF
FERRITIC STAINLESS STEELS

R.D. DAVIES and F.P.A. ROBINSON

University of Witwatersrand,
South Africa

SUMMARY The effect of vanadium (in the concentration range of 1 - 6%) alone and in combination with other
elements such as titanium, niobium, nickel, copper, molybdenum and silicon (maximum concentration of
2% each) was examined in low-interstitial 18% chromium ferritic stainless steels (C + N = 84 - 168ppm).
Vanadium was found to increase the tensile strength and lower the ductile-to-brittle transition
temperature, but reduce ductility. Stabilization with titanium produces the opposite effect on the
transition temperature when compared to the unstabilized alloy, with the temperature decreasing in the 9%
vanadium alloy. Vanadium also improved the pitting resistance of
the alloys in polarization tests in 0.1N NaCl, are when combined with titanium in the FeCl₃ immersion test.

1 INTRODUCTION

The main drawbacks to the more widespread use of
ferritic stainless steels are their poor resistan-
ce to pitting corrosion and to reducing acids,
susceptibility to weld decay and poor impact
properties. The development of low interstitial
molybdenum-bearing ferritic stainless steels
(e.g. Type 444) has effectively solved the
pitting problem, but additional improvements,
especially in the mechanical properties, are
necessary before the ferrites seriously challenge
the austenitic stainless steels. Ferritic stain-
less steels possess important properties, such as
resistance to stress-corrosion cracking and
possible cost effectiveness because of a lower
alloy content when compared to the austenites,
which makes the development of improved ferritic
steels an attractive and continuing challenge.
The present study is aimed at finding alloying
element combinations that will benefit both the
mechanical and corrosion resistant properties of
ferritic stainless steels. Another objective of
the study is to examine potential replacements for
molybdenum since this element is not widely dis-
tributed in economic quantities throughout the
world; hence the use of vanadium.

The literature contains few references regarding
the effect of vanadium in stainless steels.
Several of these references (Tomashov et al, 1964;
Biefer, 1970 ; Climax Molybdenum) show, however,
that vanadium, especially in the range 5 - 5 %,
has a beneficial effect on the pitting resistance
of both austenitic and ferritic stainless steels.
The only drawback to adding vanadium would appear
to be that it does not inhibit intergranular
corrosion (in concentrations of less than 3%)
(Lula et al, 1954; Monypenny, 1964; Climax Moly-
bdenum). Concerning the effect on mechanical
properties, vanadium was found to be beneficial in
lowering the ductile-to-brittle transition temper-
ature (Climax Molybdenum; Abrams, 1977) and in
improving weld ductility (Gipos et al, 1972) in
ferritic stainless steels. Thus, vanadium
appears to show promise as an alloying element in
stainless steels from the viewpoint of both the
mechanical properties and corrosion resistance.
In this study other element combinations with
vanadium were also examined in an attempt to
obtain improvements in specific directions - e.g.
nickel (reducing acids and impact properties);
titanium and niobium (intergranular corrosion);

molybdenum and silicon (pitting resistance), and
copper (reducing acids).

2 EXPERIMENTAL PROCEDURES

2.1 Materials

Fifteen vanadium-bearing ferritic stainless steels
were prepared by vacuum induction melting at the
University of Sheffield (U.K.). The chemical
compositions of the alloys are given in Table 1.
After casting, the alloys were hot rolled from
1050°C to a thickness of 12mm and then annealed at
between 375 and 950°C for 30 minutes, followed by
water quenching. The particular annealing
temperature chosen was experimentally determined to
obtain a fully recrystallized structure. Specimens
for mechanical testing were cut directly from the
annealed plate.

2.2 Tensile and Impact Testing

Tensile testing was carried out according to
B.S.18(1971) using 5.64mm diameter specimens.
Impact tests were performed on a Karl Frank Type
580 Charpy impact tester with a maximum breaking
energy of 294 Joules, using full-size (10mm square)
specimens to B.S.131(1972). Specimens were cut
with their length parallel to the rolling direction
and the V-notch in the through-thickness plane.

2.3 Pitting Tests

Electrochemical and immersion tests were carried
out to determine susceptibility to pitting
corrosion. The pitting potential was determined
by polarization in a deaerated 0.1N NaCl solution
at three temperatures, namely 31, 59 and 91°C. A
scanning rate of 200µV/sec was used and the pitting
potential was taken at a value corresponding to a
current density of 10µA/cm². Pitting using weight loss
as an indicator was carried out by immersion in a
FeCl₃ solution for 72 hours at room temperature, in
accordance with ASTM standard G48-76.

3 RESULTS AND DISCUSSION

3.1 Mechanical Properties

3.1.1 Tensile properties

The results of tensile testing are shown in Table I,

The Effect of Vanadium and Other Elements on the Mechanical and Corrosion Resistant Properties of Ferritic Stainless Steels.

TABLE I

MECHANICAL PROPERTIES OF STAINLESS STEELS EXAMINED IN THIS STUDY

Steel number	Nominal composition (%)(a)	TS/(CxN) (ppm/ppm)	YS(b)	UTS(b)	% Elongation in 25mm	% Reduction in area	Hardness (VHN)	ASTM grain size	Transition temperature (°C)(c)
31	1V	~/94	288.6	423.0	35	85	150	1 - 4	85.5
55	1V-Ti	700/117	22.	74.1	24	81	132	3 - 4	46.5
58	1V-Ti-1Ni	900/95	292.	5.1	23	85	150	4	38
32	2.6V	~/157	268.9	419.2	20	83	151	1 - 4	70.5
56	2.6V-Ti	700/110	261.0	402.6	27.5	75	143	4	71.5
59	2.6V-Ti-1Ni	1000/124	305.6	420.7	24	81	154	3 - 4	71.5
33	4V	~/149	339.3	469.1	22	58	159	>1	27
34	4V-Nb	900/150	318.4	46?	25	63	164	1 - 4	32.5
57	4V-Ti	1100/131	280.0	4.	24	83.5	150	3 - 4	92
40	4V-Ti-1Ni	1200/143	342.5	4.	21.5	82	156	3 - 4	98
77	4V-Ti-1.5Ni	1100/146	371.7	482.	25	75	171	3 - 4	78
41	4V-Ti-2Ni	1200/112	385.4	474.3	20.5	82	168	4	80
76	4V-Ti-1.5Ni-Si	1200/168	466.6	571.4	17	75	211	3	84
79	4V-Ti-1.5Ni-Cu	1200/84	421.6	503.4	28	80	181	3	74.5
78	4V-Ti-Ni	1100/121	311.2	454.7	28	78	171	5	98

(a) Vanadium and nickel concentrations rounded off to the nearest 0.2 and 0.05% respectively. Samples 76, 79 and 78 contain Si = 1.48%; Cu = 1.05%; and Mo = 0.86% respectively. Sample 34 stabilized with niobium only. Chromium concentration = 17.5 - 18.2.

(b) YS (0.2% proof stress) and UTS expressed in MNm^{-2} (40.1 MNm^{-2}). Specimens 33, 34, 76, 77, 78 and 79 broke outside extensometer gauge length of 25mm.

(c) Charpy transition temperature corresponding to an impact energy of 100 Joules. Error in the temperature quoted is estimated at 1 - 4°C.

together with hardness, grain size and impact measurements. Since the interstitial element content and grain size are essentially constant, the variation in tensile properties can be ascribed largely to variations in the alloying additions. The trends shown by the data in general conform with results reported in the literature. Increasing the vanadium content from 1 to 4% increases the yield and tensile strengths, although a slight decrease is apparent at the 2.6% level. Ductility decreases in the same direction while the hardness increases. These variations can be related to the solid solution strengthening effect of vanadium. Much the same trends have been reported for vanadium (and molybdenum) by Climax Molybdenum (see also Table I for the effect of molybdenum).

It has been shown (Climax Molybdenum) in a comparison of stabilised Type 444 alloy with the equivalent alloy containing vanadium (i.e. without molybdenum) that the latter provides slightly lower tensile values but significantly improves the ductility. The addition of titanium to the vanadium alloys reduces the tensile strength and hardness and has a generally detrimental effect on ductility. (It may be noted that Climax Molybdenum found stabilisation in Type 444 to be slightly beneficial in all respects compared to the unstabilised alloy). It is possible that excess titanium is leading to the formation of a grain boundary carbide or carbonitride phase although the Ti/(C + N) ratio of 6 in the V-Ti alloys is well within the 6 - 10 limit specified for mean low-interstitial alloys. (Also et al, 1977; Steigerwald et al, 1977). Pollack (1974), however, in a study of a 26% chromium low-interstitial alloy, found that a small increase in this ratio from 6 to 9.4 resulted in a significant decrease in ductility compared to an alloy with a ratio of 5. Undoubtedly vanadium, also a carbide former, is a complicating factor.

In contrast to titanium, niobium has very little effect on the tensile properties although improving the ductility slightly. This difference may be ascribed to the different form shown by the niobium precipitates (Steigerwald et al, 1977).

Regarding the effect of other elements, nickel increases the yield and tensile strengths; silicon likewise increases the values but much more substantially, while at the same time reducing ductility; copper raises the yield and tensile strength but has little effect on ductility; and molybdenum decreases the tensile values slightly.

3.1.2 Impact properties

The Charpy V-notch temperature corresponding to an impact energy of 100 Joules is given in Table I for all the alloys, with curves obtained for some of the alloys shown in Figure 1. The steep form of the curves in the figure also holds for those alloys not illustrated. In none of the alloys was it possible to obtain an upper shelf energy value because of the limitation imposed by the Charpy tester. Upper shelf values are not reported in the literature for full-size Charpy V-notch determinations of low-interstitial ferritics, but are known to exceed 570 Joules as reported for Type 444 alloys (Steigerwald et al, 1977).

Examination of the impact data shows some very interesting trends. Considering vanadium addition alone, it is seen (Figure 1) that the transition temperature decreases significantly as the percentage of vanadium increases, to the extent that at a vanadium level of 4% the alloy is ductile within a few degrees of room temperature. (In fact transverse Charpy specimens of alloys 33 and 34, as tested by Sheffield University, were ductile at a room temperature of 22°C). Stabilization with titanium, however, produces the opposite effect then the 4% vanadium alloy showing a much lower transition temperature (47 C) than the 4% vanadium alloy (52°C). In contrast, niobium has only a slightly detrimental

94

R.R. GANES and F.P.A. ROBINSON

The ... of Vanadium and other Elements in the Mechanical and Corrosion Resistant Properties of ... le Stainless Steels

Fig. 1. ...arpy impact results for some stabilised and unstabilised vanadium-bearing 18% chromium stainless steels. Shown in dashed lines are comparison with unstabilised and unstabilised Type 444 alloys (...V = 0.0%) (Steigerwald et al., 1977).

effect on the formation temperature in the 9% vanadium alloy.

Interpretation of the trends shown is somewhat difficult in view of the lack of published data on carbide phases present in the Fe-Cr-V system. Chin and Quarrell (1...) have examined carbide formation in a tempered 12% vanadium, 0.5% carbon steel and found that $Cr_{23}C_6$ only formed up to a vanadium content of V.5%. From V.5 to 9% (the maximum vanadium level studied) a mixture of M_6C and $M_{23}C_6$ compounds formed. Above a certain concentration of 8.5%, corresponding to a vanadium level of 9%, V_4C_3 formed. It is rather hoped that chromium and vanadium are effectually interchangeable in the chromium carbides formed in these steels. Silcock (1973) found that vanadium (up to 5.5%) in a 18Cr-12Ni alloy reduced ductility, in the hardened condition due to the continuous carbide network found at the grain boundaries. The Al, in the present work have much lower interstitial levels and a higher chromium content and, in the untempered condition, will probably show a very different carbide phase pattern. One explanation for the trends shown by the unstabilised data could be that chromium carbide in the dominant carbide at low vanadium levels and is proving detrimental to the impact properties. At higher vanadium levels, vanadium carbide is the dominant phase and appears to be beneficial. In the case of the titanium stabilised alloys, it would appear that titanium is acting according to the vanadium level. Titanium is well known to have a detrimental effect on the impact properties of low-interstitial ferritic steels as steels, especially when present in excess. Abo et al., 1977; Steigerwald et al, 1977). In the present study, titanium and vanadium are reacting for the carbide in the alloy, resulting in a complex situation. Abo et al (1977) found that titanium inhibits the grain boundary precipitation of carbonitrides and thus tends to work effectively in the microstructure. It was suggested that TiN inclusions were acting as crack initiation sites similar to grain boundary precipitates. In contrast, niobium is less detrimental than titanium, a fact which has been ascribed to the different form and distribution taken by the carbide and nitride precipitates of these two elements (Steigerwald et al, 1977). The precipitates in the niobium alloys were found to be relatively small and finely dispersed.

A similar situation was found for the precipitates in the unstabilised alloys in this study.

An optical and electron examination of the fracture surfaces and polished sections of the alloys has not enabled a complete explanation to be formulated for the impact trends shown. Optical examination of polished surfaces shows largish square-shaped carbides and other precipitates scattered throughout the ferrite, in amounts depending on stabilisation. The unstabilised and niobium-stabilised alloys show few to very few precipitates whereas the titanium-stabilised alloys show a fair number of precipitates. There does not appear to be significant grain boundary precipitation but this would be difficult to confirm optically in such low-interstitial alloys. SEM examination of the ductile fracture surfaces shows small square-to angular-shaped precipitates, 2 to 4 μm in size, at the base of the dimple structures. EDX analysis of 29 precipitates, mostly of the type just described, showed them to be composed mostly of titanium and vanadium (noted together 15 times). Aluminium was detected in 14 precipitates and chromium in four. Other elements detected in the precipitates included phosphorus, chlorine and sulphur. The unstabilised alloys contained smaller precipitates compared to the titanium stabilised alloys, thus confirming the optical microscopy results. In the case of the niobium-stabilised alloys the few precipitates seen were too small to analyse. The precipitates in the fracture surfaces do not appear to be representative of the total precipitate population since 12 out of 26 precipitates examined in surfaces pitted in polarisation studies in NaCl contained the chromium-vanadium combination.

The brittle fracture surfaces show a dominant trans-granular fracture mode with very little evidence of intergranular fracture. Evidence that some fracture had been initiated by grain boundary precipitates is shown by the presence of ridges containing scattered pits, none of which still retain precipitates.

Regarding the effect of other elements on the impact properties of the alloys, nickel was found to be variable but in balance lowered the transition temperature, copper lowered the transition slightly, and molybdenum and silicon raised the temperature. Climax Molybdenum found that vanadium lowered the transition temperature to a much greater degree than molybdenum in Type 444 alloys, and ascribed this to the grain refining properties of vanadium. Aslund (1977) confirmed the beneficial effect of vanadium on the impact properties of Type 444 molybdenum-bearing alloys (containing 1.7% vanadium) but found that additional stabilisation with 0.35% titanium proved detrimental. It is probable, considering the results of the present study, that excess titanium stabilisation is the cause of the poor impact properties.

In summary, it can be concluded that titanium-vanadium precipitates in the matrix are largely responsible for the brittle fracture of the alloys. At a constant titanium level, increasing the vanadium beyond 2.6% proved detrimental although this is not the case for the alloy stabilised with niobium.

3.1.5 Corrosion properties

The results of electrochemical and ferric chloride pitting tests are shown in Table II.

The results confirm previous work (Tomashov et al, 1964; Climax Molybdenum) where it was found that vanadium improved the pitting resistance of stainless steels. The pitting potential increases with

95

The Effect of Vanadium and Other Elements on the Mechanical and Corrosion Resistant Properties of
Ferritic Stainless Steels

TABLE II

PITTING CORROSION OF STAINLESS STEELS IN THIS STUDY

Steel number	Nominal composition	Pitting potentials (mV)(a) 31°C	59°C	81°C	Weight loss (b) (mdd)
31	1V	200	71	20	1764
35	1V-Ti	129	105	36	1874
38	1V-Ti-1Nb	85	96	76	1965
32	2.6V	285	87	52	2607
36	2.6V-Ti	195	155	83	670
39	2.6V-Ti-1Ni	157	183	120	2133
33	4V	504	197	113	1942
34	4V-Nb	442	254	198	620
37	4V-Ti	327	227	170	115
40	4V-Ti-1Ni	341	230	191	665
77	4V-Ti-1.5Si	408	218	165	390
41	4V-Ti-2Ni	270	224	154	316
76	4V-Ti-1.5Si-Si	464	230	142	42.9
79	4V-Ti-1.5Si-Cu	292	13	178	1581
78	4V-Ti-Mo	595	3	272	2.5
Type 430		-58	-19	-320	4520
Type 316		54	-100	77	97(c)
Type 444		430	—	—	1250(c)

(a) mV versus SCE
(b) Weight loss in 10% FeCl₃, 6H₂O at 25°C.
(c) From Steigerwald (1974)

the vanadium content, a feature noted at all the
temperatures tested. Stabilization is slightly
detrimental at 31°C but improves the pitting poten-
tial at 59 and 81°C, with niobium being better than
titanium. Regarding the effect of other elements,
nickel and copper are beneficial only at the higher
temperatures, silicon shows the opposite effect,
while molybdenum is very beneficial.

The work of Climax Molybdenum showed that in Type
444 alloys vanadium (without molybdenum) produced
a higher pitting potential than the equivalent
molybdenum content. Aslund (1977) reported that
the addition of only 0.5% vanadium to a Type 444
molybdenum alloy increased the pitting potential
by 125mV.

SEM examination of the pitted surfaces of the polar-
ization specimens showed that precipitates and sur-
face scratches were often observed to be the sites
for pit initiation. Once pitting was initiated it
could clearly be seen to be working along the grain
boundaries in the alloy. EDS analysis of precipi-
tates in the pits revealed the presence of silicon,
chromium, vanadium and aluminium with each being
counted 12 times in 26 precipitates. Chromium and
vanadium were always noted together. Calcium, pot-
assium and sulphur were also detected. Weight loss
measurements in FeCl₃ confirm most of the trends
found in the polarization study. Vanadium, however,
was found to be slightly detrimental. Nickel, sili-
con and molybdenum were beneficial while copper was
detrimental. Titanium proved to be more beneficial
than niobium which is the reverse of the result
obtained from the pitting potentials.

4 CONCLUSIONS

The results of the study show that vanadium
benefits both the mechanical properties and the
resistance to pitting corrosion of ferritic stain-
less steels. If the results of Climax Molybdenum
which show that a vanadium content of at least
3% is needed to prevent intergranular corrosion in
the Strauss test are confirmed, then the most

promising alloy combination would be a 4% vanadium
alloy, with or without niobium. Another alloy
offering good mechanical properties is one contain-
ing 4% vanadium, 1.5% nickel -titanium. The
pitting resistance of this alloy, however, is poor
and some molybdenum (say 1%) would be needed,
provided the nickel-molybdenum combination does not
promote susceptibility to stress-corrosion cracking.

6 REFERENCES

ABO, H., NAKAZAWA, T., TAKEMURA, S., OGOYAMA, M.,
OGAWA, H. and OKADA, H. (1977). The role of carbon
and nitrogen on the toughness and intergranular
corrosion of ferritic stainless steels. Proc. Conf.
Stainless Steel 77, (Climax Molybdenum), London,
pp 35-47.

ASLUND, C. (1977). Properties and applications of
low interstitial 18 and 25% Cr-Mo ferritic stain-
less steels. Proc. Conf. Stainless Steel 77,
(Climax Molybdenum), London, pp 175-176.

BIEFER, G.J. (1970). Effects of alloying on
polarisation and corrosion of Type 430 stainless
steel. Canad. Met. Quart., Vol. 9, pp 537-550.

CLIMAX MOLYBDENUM, U.S.A.   Private communication.

BOLA, M.A., LENA, A.J. and KIEFER, G.C. (1954).
Intergranular corrosion of ferritic stainless
steels. Trans. AIM, Vol. 46, pp 97-103.

MONTMRORY, J.H.G. (1954). Stainless Iron and Steel.
London, Chapman and Hall. Vol. 1, pp 243-246.

POLLARD, B. (1974). Effect of titanium on the
ductility of 26% chromium, low interstitial
ferritic stainless steel. Metals Tech., Vo. 1,
p1 31-36.

SHAW, J.W.R. and QUARRELL, A.G. (1957). The form-
ation of carbides in low-carbon, chromium-vanadium
steels at 700°C. JISI, Vol. 185, pp 10-22.

SILCOCK, J.M. (1973). Precipitation in austenitic
steels containing vanadium. JISI, Vol. 211,
pp 792-800.

SIMCO, D.J., STRIEGERWALD, R.F. and WHITCOMB, N.E.
(1972). Ductile corrosion-resistant ferrous alloys
containing chromium. U.S. Patent no. 3672876,
June 27.

STEIGERWALD, R.F. (1974). New molybdenum stainless
steels for corrosion resistance: a review of recent
developments. Mat. Performance, Vol. 13, pp 9-16.

STEIGERWALD, R.F., DUNDAS, H.J., PEDERSON, J.D. and
DAVISON, R.M. (1977). The physical metallurgy
of Fe-Cr-Mo ferritic stainless steels. Proc. Conf.
Stainless Steel 77, (Climax Molybdenum), London,
pp 57-77.

McCARDEN, N.D., CHERNOVA, G.P. and MARKOVA, O.N.
(1964). Effect of supplementary alloying elements
on pitting corrosion susceptibility of 18Cr-14Ni
stainless steel. Corrosion, Vol. 20, pp 1665-1731.

THE EFFECT OF REPLACING MOLYBDENUM WITH VANADIUM ON THE
CORROSION RESISTANT PROPERTIES OF STAINLESS STEELS

R.D. Davies, C.J. Gross, P. van Biljon and F.P.A. Robinson

Department of Metallurgy,
University of the Witwatersrand,
1 Jan Smuts Avenue, Johannesburg, South Africa

ABSTRACT

The effect of replacing molybdenum with vanadium, both fully and partially, on
the corrosion resistant properties of wrought ferritic, and wrought and cast
austenitic stainless steels is examined. All alloys contained approximately
14% chromium with the austenitic alloys based on Types 304 and 316
respectively. The ferritic alloys contained chromium and 1-4% vanadium; the
wrought austenitic alloys up to 6% vanadium and 2% molybdenum (not in combi-
nation); and the cast austenitic alloys up to 6% vanadium and 1.5% molyb-
denum, separately and in combination. Corrosion testing involved anodic
polarization in H$_2$SO$_4$ and determination of the pitting potential in 0.1N
NaCl. Vanadium was found to improve the pitting resistance of all alloys in
NaCl, and generally had a beneficial effect on the passivation character-
istics of the ferritic and wrought austenitic alloys in H$_2$SO$_4$. The element
had a detrimental effect on porosity in the cast austenitic alloys, a fact
possibly related to the higher carbon and nitrogen level and the formation of
detrimental precipitating phases (e.g. carbides).
Molybdenum was found to be more effective than vanadium on a weight-for-
weight basis in conferring corrosion resistance.

KEYWORDS

Molybdenum replacement; vanadium; ferritic; austenitic stainless steels;
corrosion properties; potentiodynamic testing; H$_2$SO$_4$; pitting potential.

INTRODUCTION

Molybdenum has a very beneficial effect on the corrosion resistant properties
of stainless steels, in particular the resistance to pitting corrosion and to
sulphuric acid. There are several factors which have encouraged the develop-
ment of a local substitute for molybdenum, these being that South Africa must
import all her requirements of the metal, the importance of the metal as an
alloying element in stainless steels and high-strength, low-alloy steels, the
highly fluctuating price of the metal, and lastly but perhaps most important-
ly, the abundance in South Africa of the metal vanadium which is one of the
most promising substitutes for molybdenum.

The literature contains several references to the fact that vanadium improves the pitting resistance of stainless steels (Tomashov and others, 1964; Biefer, 1970; also Climax Molybdenum, unpublished data), particularly in the concentration range 2-5%. An additional advantage of vanadium in ferritic stainless steels is the improvement it confers on the impact properties, an aspect in which these steels are very deficient (Aslund, 1977; Davies and Robinson, 1982).

The object of the present investigation was to examine the effect of replacing molybdenum with vanadium, both fully and partially, on the corrosion properties of ferritic and austenitic stainless steels. Polarization tests were conducted to determine the resistance to pitting in a NaCl solution, and the passivation characteristics studied in H_2SO_4. An alloy containing 18-19% chromium was used as a base for alloying additions.

EXPERIMENTAL PROCEDURES

Materials. The compositions of the alloys tested are listed in Table . The wrought ferritic and austenitic stainless steels were both prepared by vacuum induction melting, the base composition being respectively a low-interstitial

TABLE 1   Chemical Composition of the 18-19% Chromium Stainless Steels Examined in this Study

Classification	Percentages		ppm	
	Vanadium	Molybdenum	Carbon	Nitrogen
Ferritic Alloys				
(18% chromium)				
1 V	1.12	–	56	44
2.6 V	2.57	–	100	57
4 V	4.00	–	90	69
Wrought Austenitic Alloys				
base alloy (Type 304L)				
(18%Cr – 9% Ni)	0.13	0.11	150	270
2 V	2.05	0.09	280	360
4 V	3.70	0.08	190	330
6 V	5.65	0.13	230	360
1 Mo	0.12	1.04	240	310
2 Mo	0.09	1.97	170	390
Cast Austenitic Alloys				
base alloy (Type CF-8)				
(18% Cr – 11% Ni)	–	–	570	
2 V	2.10	0.80	490	
4 V	4.16	0.25	500	
6 V	6.04	0.13	530	300-400
3 Mo	0.09	2.91	360	
2 V – Mo	2.10	1.62	570	
2.7 V – Mo	2.69	1.41	480	

Minor element concentrations (P, S, Si, etc.) in the austenitic alloys are as reported for the base Type alloys. For the ferritic alloys the levels were somewhat lower, viz. P = 0.012%, S = 0.008%, Si = 0.05%.

element 18% chromium alloy and Type 304L. The ferritic alloys were hot-rolled from 1050°C to a thickness of 12mm before being annealed at 825-875°C for 30 minutes, and water quenched, while the wrought austenitic alloys were hot-rolled from 1200°C to a thickness of 12mm, followed by a solution treatment at 1050°C for 30 minutes and water quenching A Type CF-8 alloy (19% Cr - 11% Ni) was used as the base composition for the cast austenitic alloys and preparation involved argon induction melting, casting and a solution treatment at 1050°C for 2 hours, followed by water quenching.

Pitting Tests. Determination of the pitting potential involved anodic polarization in a deaerated 0.1N NaCl solution at a temperature of 30°C. The sample was allowed to stabilize for one hour in the NaCl solution before commencing at a scanning rate of 200 µV/s from the free corrosion potential. The actual pitting potential was taken at a value corresponding to a current density of 10 µA/cm², as suggested by Truman (1978).

Passivation Tests. Passivation characteristics were determined using accepted potentiodynamic testing procedures involving polarization in deaerated 1N H_2SO_4 (for the ferritic and wrought austenitic alloys) and 2N H_2SO_4 (for the cast austenitic alloys). The same size samples and preparation and running procedures as for the determination of the pitting potentials were followed with the exception that cathodic activation was carried out before anodic polarization. In the case of the wrought alloys the samples were cathodically activated at -650 mV (versus the SCE) before the stabilization period, whereas for the cast alloys the polarization run was commenced at 500 mV below the free corrosion potential.

RESULTS AND DISCUSSION

The data obtained for three selected points on the anodic polarization curve in H_2SO_4 and for the pitting potential in NaCl, are given in Table 2. Plots examining some trends from the data are shown in Figures 1 and 2.

Pitting Results. Examination of Table 2 shows that vanadium increases significantly the pitting potential in NaCl, thus confirming in detail the results reported by other workers. The pitting potential increased continuously in the austenitic alloys as the vanadium level was raised above the base alloy composition. Although a base alloy was not examined in the case of the ferritic alloys, the same trend is envisaged. A comparison with the basic austenitic alloys containing molybdenum showed that this element was more beneficial than vanadium on a weight-for-weight basis by a factor of about two. A comparison of the vanadium-bearing ferritic alloys with Type 44S stainless steel, an 18% Cr - 2% Mo - Ti stabilized alloy with an interstitial element level about 2 - 3 times that reported for the ferritic alloys here, also showed molybdenum to be more effective than vanadium. SEM examination of the alloys, combined with EDX analysis, showed that pitting was initiated at inclusions such as silicates, oxides and sulphides.

The combination of vanadium with molybdenum also had a beneficial effect on the pitting potential in the cast austenitic alloys, in particular when combined in the proportion 2.7% vanadium and 1.4% molybdenum. The alloy with this combination had a pitting potential almost as high as the 6% vanadium alloy, again showing the greater effect of molybdenum.

Passivation Results. The anodic polarization results obtained in H_2SO_4 for the wrought vanadium-bearing ferritic and austenitic alloys differ significantly from those obtained for the cast austenitic alloys. Whereas vanadium had a generally beneficial effect in promoting passivity in the wrought

alloys, it was detrimental in the cast materials. The most noticeable effect of vanadium in the ferritic and wrought austenitic alloys was in reducing the critical density and potential for primary passivation (Fig. 1). On balance, *the effect on the passive region was beneficial* (i.e. the passive potential range was extended and the passive current density lowered), except in the ferritic alloys where vanadium appeared to lower the breakdown potential. This trend, as shown in Fig. 1, is due to incipient breakaway of the trans-passive region.

TABLE 2 Anodic Polarization Results in H_2SO_4 and 0.1 NaCl, at 30°C

Alloy	E_c^*	E_{cp}	I_p	E_p	I_b	E_b	E_{pit}^{**}
FERRITIC ALLOYS (1N H_2SO_4)							
Type 430	18766	-411	24	-178	3.9	+713	-58
1 V	36621	-423	19	-263	7.8	+720	+200
2.6 V	19549	-435	18	-274	7.9	+567	+285
4 V	10351	-471	15	-292	6.3	+451	+504
WROUGHT AUSTENITIC ALLOYS (1N H_2SO_4)							
Base alloy	1610	-270	49	-92	85	+779	+201
2 V	1140	-325	23	-123	13	+800	+210
4 V	1030	-329	18	-133	11.1	+790	+220
6 V	841	-350	20	-160	9.5	+795	+232
1 Mo	80	-280	6.1	-115	8.5	+825	+262
2 Mo	96	-273	6.3	-170	5.8	+830	+281
CAST AUSTENITIC ALLOYS (2N H_2SO_4)							
Base alloy	45	-262	4.7	-100	4.0	+871	+143
2 V	51	-251	4.9	-86	4.9	+771	+214
4 V	126	-258	6.0	-100	7.5	+700	+293
6 V	870	-267	15	-93	8.5	+450	+379
3 Mo	18	-239	4.5	-100	4.0	+871	+421
2V-Mo	12	-219	4.7	-79	5.4	+771	+285
2.7V-Mo	17	-219	5.1	-66	4.7	+714	+345

* Refer to Fig. 1 for abbreviations. I in $\mu A/cm^2$, E in mV.

** E_{pit} = pitting potential (mV) in 0.1N NaCl.

The potentials reported are relative to the Standard Calomel Electrode, with each result being the average of 1-4 determinations.

A basic, low-interstitial, 18% chromium ferritic alloy without vanadium was not examined in this study but comparison of the critical current density with results for Type 430 and other 18% chromium alloys (Fig. 2) shows that vanadium is in fact detrimental up to a concentration of several percent. An increase in vanadium beyond the 1% level, however, was found to be beneficial in reducing the critical current density.

A comparison of the vanadium- and molybdenum-bearing wrought austenitic alloys shows that molybdenum was in most cases more beneficial than vanadium, especially in reducing the critical current density (Fig. 2). Molybdenum, however, was not as effective as vanadium in reducing the critical potential for primary passivation.

The effect of vanadium in the cast austenitic alloys was to increase the

critical current density (Fig. 2) and to contract the potential range of the
passive region and move it to higher current values. As was the case for the
ferritic alloys, vanadium in the cast alloys decreased the breakdown potential
in H_2SO_4. The detrimental effect of vanadium in the cast alloys may be due
to the high carbon level of 550ppm (relative to the wrought austenitic alloys)
causing the precipitation of some harmful phase, such as a carbide. Tomashov
and others (1964), however, found vanadium to be beneficial with a carbon
level of 360ppm. It is possible that the formation of ferrite in the cast
alloys is contributing in some way to the poorer passivation characteristics
shown, although this is not the case for the wrought austenitic alloys which
show a similar increase in ferrite phase with increasing vanadium content.
Microprobe analysis has confirmed the results of previous work (Forbes-Jones
and Kain, 1975; Dundas and Bond, 1975) that ferrite is enriched in chromium,
molybdenum and vanadium relative to the austenite.

An important difference between molybdenum and vanadium as alloying elements
is that molybdenum occurs largely in solid solution whereas vanadium occurs
both in solid solution and as a precipitate (hence the use of vanadium as a
stabilizer by Aslund, 1977). More research is needed on the nature of pre-
cipitating phases as related to the vanadium and carbon and nitrogen levels
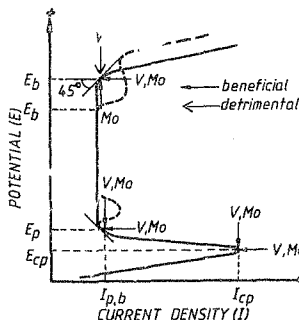to clarify the results in the austenitic stainless steels.

Fig. 1. Effect of vanadium and molybdenum on the passi-
vation characteristics of wrought ferritic and
austenitic stainless steels in 1N H_2SO_4 (from
this study).

cp = critical values for primary passivation;
p = primary values for passivation;
b = breakdown values.

CONCLUSIONS

Vanadium is found to improve the pitting resistance of ferritic and austen-
itic stainless steels in NaCl, and the passivation characteristics in general
of the wrought ferritic and austenitic alloys in H_2SO_4. The element has a
detrimental effect on passivity in H_2SO_4 in the cast alloys possibly due to
the high carbon and nitrogen level which is leading to the formation of harm-
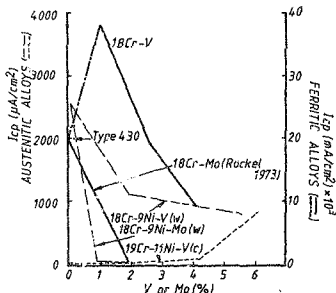ful precipitating phases. More research is needed to clarify this point.

Fig. 2. Effect of vanadium and molybdenum on the critical
current density (Icp) for 18-19% chromium stainless
steels in 1N H_2SO_4 (2N H_2SO_4 for cast alloys).

(w) = wrought alloys; (c) = cast alloy.

ACKNOWLEDGEMENTS

REFERENCES

Aslund, C. (1977). Proc. Conf. Stainless Steel '77, (Climax Molybdenum),
  London, 173-176.
Biefer, G.J. (1970). Canad. Met. Quart., 9, 537-550.
Davies, R.D. and F.P.A. Robinson (1982). Aust. Institute Metals, Annual
  Conf. Proc., Sydney, 93-96.
Dundas, H.J. and A.P. Bond (1975). Corrosion 75, NACE, USA, 156 1-11.
Forbes-Jones, R.M. and R.M. Kain (1975). Corrosion 75, NACE, USA, 67/1-26.
Rockel, M.B. (1973). Corrosion, 29, 393-396.
Tomashov, N.D., G.P. Chernova and O.N. Marcova (1964). Corros on, 20, 166t-173t.
Truman, J.E. (1978). Stainless Steel Industry, 6, 21-26.

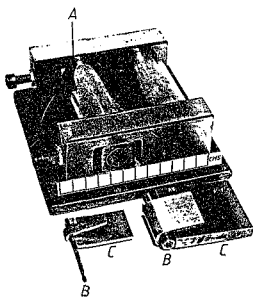## NEW APPARTUS FOR PREPARING U-BEND SPECIMENS

R.D. DAVIES, Department of Metallurgy, University of the Witwatersrand,
1 Jan Smuts Avenue, Johannesburg, South Africa.

Many different types of apparatus have been used by research workers
to prepare U-bend specimens for stress-corrosion cracking experiments.
Most of these, although simple in design, are not very versatile and
usually can only bend material of limited dimensions through a certain
fixed diameter and at a rate depending on the person doing the bending.
The present article describes an apparatus that is versatile in that
specimens varying widely in size can be bent through various diameters
and at a constant and reproducible rate by the use of a hydraulic press.
In addition, the apparatus can be used for bending specimens through very
small diameters as may be required for the Strauss intergranular corrosion
test.

The apparatus is shown in the accompanying photograph. As can be seen,
the rollers (A) can be adjusted laterally to take material of different
thickness, as well as bending rods (B) of varying diameter. In operation,
the specimen to be bent is placed squarely on the rollers, the rod around
which the specimen is to be bent placed centrally above, and a pusher
plate (C) placed vertically on top of the rod. The ram from a hydraulic
press pushes down on the pusher plate, thus causing the specimen to
be bent. By using an automatic press the conditions under which
specimens are bent can be controlled fairly closely, a fact which reduces
the number of variables to be accounted for in considering the precision
of the time obtained in the subsequent stress-corrosion cracking experiments.
In the case of very elastic material with considerable springback, a
vertical slot can be cut out of the end of the pusher plate where it
rests on the pusher rod thus enabling a bolt to be inserted to hold
the bent sides of the specimen together.

In addition to producing more reproducible results, the apparatus can
be used for bending specimens through very small diameters. The author
has successfully bent specimens through diameters of 2-3mm for the
Strauss intergranular corrosion test (see photograph). In this case the
pusher plate must be narrow enough to allow the sides of the specimen
to be brought parallel.

In constructing this apparatus, the size of the components will depend on the general range of specimen sizes to be expected in the preparation of U-bend specimens. It is suggested that the apparatus described in this paper be considered as a standard for preparing U-bend specimens for stress-corrosion cracking experiments in order to obtain more reproducible results.

Apparatus for preparing U-bend specimens. A = adjustable roller ;
B and C = pusher rod and plate respectively.

Author Davies Ronald Douglas
Name of thesis The Effect Of Vanadium And Other Elements On The Mechanical Properties And Corrosion Resistance Of Ferritic Stainless Steels. 1983