WELDING OF FERRITIC AND MARTENSITIC 11-14%Cr STEELS

This document is dedicated to the memory of

Dr Trevor Gooch,

friend and colleague,

who, as Chairman of Sub-Commission IX-H throughout the early 1990's, initiated
the work and provided much constructive comment and positive support.

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BY

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1. INTRODUCTION

The commercial history of stainless steel began with Brearly's air-hardening 'cutlery' steel, a direct ancestor of the fully martensitic 0.2%C-12%Cr alloy now commonly known as type 420. Since the late 1970s, this alloy has been rediscovered and has rapidly displaced carbon steel (plus corrosion inhibitors) for downhole tubulars in oilfield applications. There are good reasons for the renewed interest in this group of materials since martensitic stainless steels can provide strength-to-weight ratio equal to high strength low alloy steels and better than duplex stainless steels, combined with useful corrosion resistance for many applications and at a relatively low cost.

The emergence of life cycle costs analysis as a formal discipline and improved steelmaking and working technologies has given stainless ferritic and martensitic steels new status, but more importantly has provoked a fresh appraisal of the economics and performance potential of "lean alloyed" stainless steel in general. The consequence of this vigorous activity has been evident in a wave of new or improved alloys based on the 10.5-14%Cr system, the leanest being the utility ferritics, having the minimum chromium level required to provide a stable passive film and the essential "stainlessness" of the alloy. As a whole, the microstructure of these alloys (loosely described 12% or 13%Cr) ranges from predominantly ferritic to fully martensitic, with the former having good resistance to stress corrosion cracking whilst the latter have the highest strength.

Effective and widespread application of any alloy is dependent upon good weldability and this factor alone has previously restricted the exploitation of ferritic and martensitic stainless steels more than any other (alloy 420, for example, is one of the few stainless steels with virtually no practical arc welding history). However, advanced steel-making technology now enables tight control of composition and can provide extremely low levels of carbon (and nitrogen) with consequent improvement in as-welded HAZ properties, as well as the reduction of chromium carbides which degrade corrosion performance.

These opportunities have not only helped to improve the weldability of utility ferritics, but have also been fully exploited in the new 'weldable supermartensitics', in which corrosion performance and mechanical properties are greatly enhanced with additional alloying. Development of optimised and economic welding procedures for supermartensitics is currently a challenging area of activity.

2. SCOPE

This review will attempt to establish the state-of-the-art as it exists at the turn of the millennium, particularly with respect to the welding and weldability of the wide range of mostly wrought 13%Cr steels and variants used primarily for combinations of ambient temperature strength and corrosion resistance. The evolution of the modern supermartensitics is still taking place and in May 1999 the first major international conference devoted to the topic took place, the results of which have been incorporated.

This review will not deal with the related but specialised steels listed below, some of which extend to higher levels of chromium where appropriate. References are given to the principal reviews for each group, although relatively few concentrate on welding:

- 'Superferritics' which typically exceed 20%Cr + Mo [1, 2, 3]

- Scaling-resistant ferritics based on 12%Cr or more with Si or Al additions – 'Fecralloys' and 'Sicromals'

- Creep-resistant martensitics based on 11-12%Cr + Mo with strong carbide formers [4, 5]
- Precipitation hardening stainless martensitics [6] and higher alloy 'controlled transformation' martensitics which require refrigeration as an essential step during heat treatment [6, 7]

With the exception of purely ferritic types, a number of alloys within the scope of this review are also available as castings. In most instances, these are welded in the same way as their wrought equivalents except that consumables of dissimilar type are generally unsuitable if postweld solution treatment is to be applied.

Applicable processes are the common arc welding processes: SMAW, GTAW, GMAW, FCAW, SAW and, for some materials, possibly PAW. The most appropriate of these will depend on a variety of factors, including availability of suitable consumables.

3. THE 13CR STEELS

For the purposes of this document, the 13%Cr steels have been divided into four sub-groups which are described as follows:

Utility Ferritics	Section 5/Table 1
Lean Martensitics	Section 6/Table 2
Soft Martensitics	Section 7/Table 3
New Supermartensitics	Section 8/Table 4A-C

For each sub-group, a table of compositions, sources and references is given in Section 5, 6, 7 or 8, together with a commentary on the group properties, range of applications, weldability and corrosion behaviour. In Figure 1, actual tensile and proof stress data are plotted, showing the differences between some representatives of these groups. For comparison, the high carbon martensitic type 420 is also included, together with some data for duplex types. Owing to similar alloying, the strength of soft martensitics is equivalent to the supermartensitics. The leanest supermartensitics are likewise equivalent to lean martensitics; strength range within each martensitic group is largely dependent on heat treatment.

4. METALLURGICAL OVERVIEW

The metallurgical context and behaviour of stainless ferritic and martensitic stainless steels are illustrated by referring to phase diagrams for the Fe-Cr system [8], as shown in Figure 2 for carbon levels of 0.01%, 0.05% and 0.1%. Although representing the equilibrium state for pure Fe-Cr-C alloys, not real industrial alloys, these show a number of features relevant to understanding base material and weld HAZ behaviour as well as that of matching or autogenous welds (and castings). A vertical section traverses the equilibrium microstructure at any temperature for a given level of chromium, and shows that 11-15%Cr alloys with sufficient carbon will experience transformation through an austenitic (γ) or partially austenitic region centred around 1000^OC. However, because these diagrams do not show the effect of cooling rate, one important influence of chromium is not apparent: chromium considerably retards the transformation of austenite to alpha-ferrite plus carbides (α+C)[**]. This has two main consequences: austenite transforms directly to martensite under practical cooling conditions, and chromium also increases the tempering resistance of this martensite.

[**]Note on terminology: alpha ferrite (α) forms by isothermal decomposition of austenite (γ) below about 800^OC, distinguishing it from the high temperature primary delta ferrite (δ), from which the austenite is formed. Over a wide range of cooling rates, austenite transforms to martensite (usually denoted M but occasionally α'). When present, carbides (C) are predominantly of the type $Cr(Fe)_{23}C_6$.
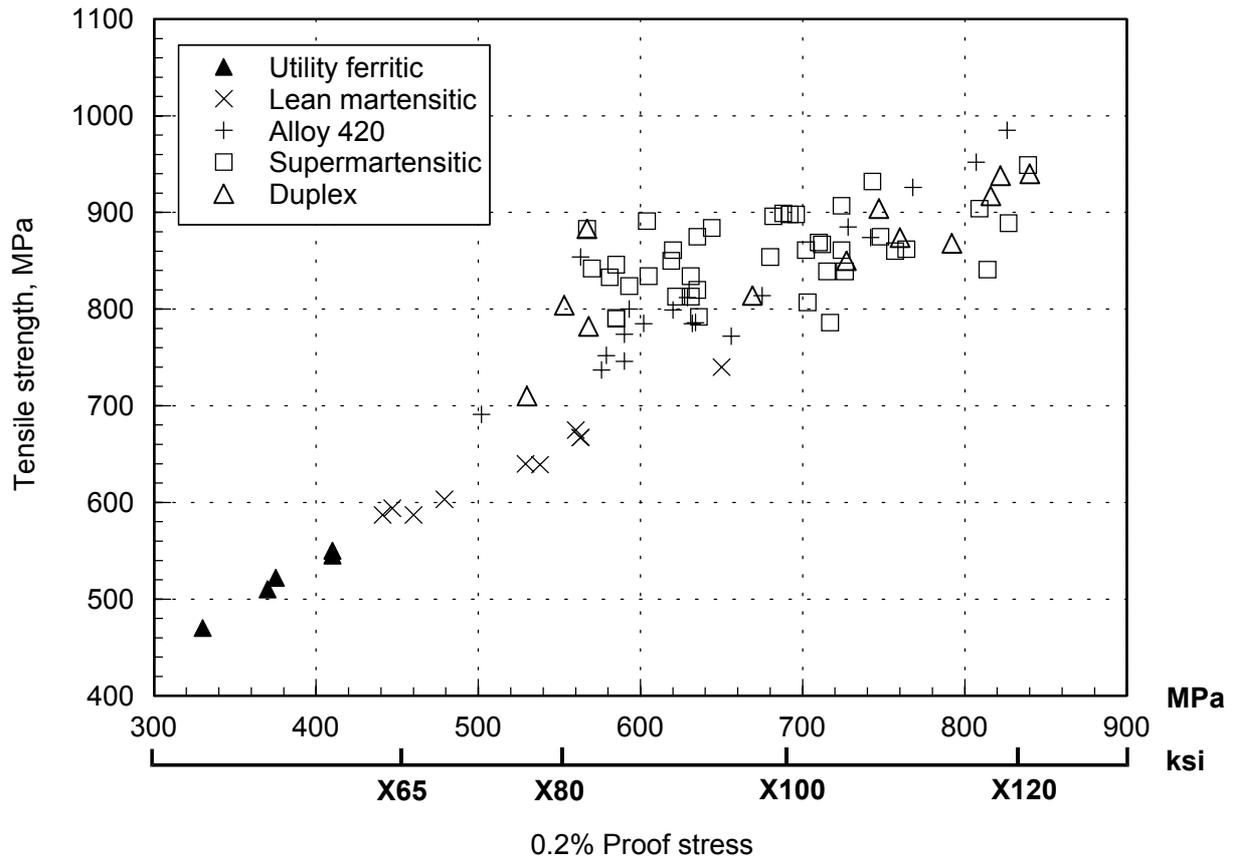
Figure 1 Relationship between 0.2% proof stress and tensile strength for ferritic and martensitic 11-15%Cr stainless steels. Data for 22-25%Cr duplex type are included for comparison. For clarity, tie-lines are not drawn, but the trend for each group is apparent. All data are for base material (various sources).
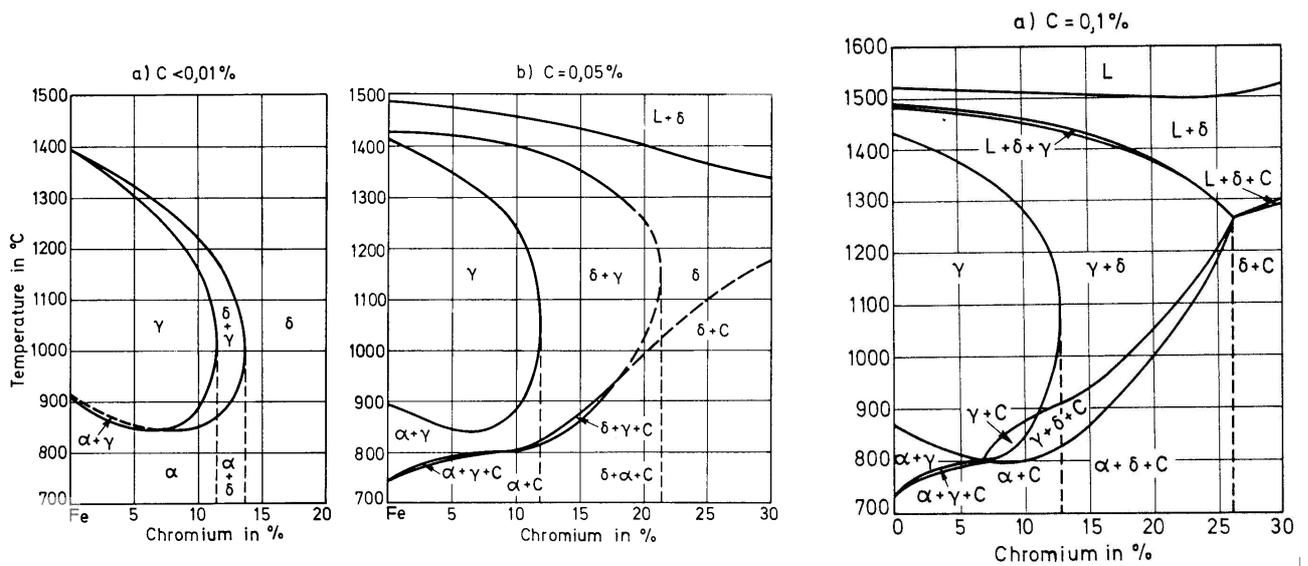

Figure 2: Ranges of γ, δ and α in the iron-chromium constitution diagram [8]

4.1 Solidification

Delta ferrite is always the primary solidification phase. The dendrite cores initially inherit carbon-depleted pure FeCr which is the first to solidify at the dendrite tips. Carbon concentrated in the last-solidifying liquid diffuses rapidly into the growing dendrites, although this homogenization may be incomplete in weld metals. Only when carbon exceeds about 0.08% is some austenite also formed at the terminal stage of solidification (the region marked L+δ+γ in figure 2c for 0.1%C alloys). In this case, the excess carbon rejected at the primary ferrite dendrites forces the interdendritic liquid to solidify as carbon-enriched austenite.

Recent and detailed solidification studies [9] on low carbon highly alloyed weld metals (martensitic 12-15%Cr with ~10% other) have shown that interdendritic partitioning of the additional solute elements (e.g. Ni, Mo, Nb, Si, Cu) occurs at the fully ferritic solidification front, but soon afterwards this microsegregation is largely eliminated by rapid diffusion. However, earlier authors [4, 10], evidently referring to high carbon and leaner alloys, claim that segregation can persist to the extent that a finally martensitic microstructure may retain ferrite originating from both carbon-depleted dendrite cores and interdendritic locations enriched with the ferrite formers Mo, Si, etc. Moreover, the highest alloy weld metals of supermartensitic type are balanced to avoid segregation caused by final austenitic solidification [11] which will occur if compositions reach the Fe-Cr-Ni peritectic range (F + FA solidification mode). The literature reveals few clear reports of hot cracking in these alloys, and although there can be no doubt that a form of solidification cracking can occur, it must be concluded that this hazard is far less likely than in, for example, austenitic stainless steel welds. Highly restrained fillet welds with a concave profile were found to be sensitive to centreline cracking [12] which was eliminated by the use of a fully martensitic 13%Cr-4%Ni type consumable. The exact mechanism has not been established, but cracking is believed to occur in the temperature range 900-1350$^{\mathrm{o}}$C where shrinkage strains cause fracture of ferrite grains or austenite-ferrite grain boundaries. It is notable that hot cracking was confined to martensitic welds with higher chromium equivalent (see Section 4.2.1), in which retained ferrite was present at room temperature.

4.2 Transformations

During further cooling, the most important feature is the influence of chromium on transformation to austenite, without which the alloy cannot be fully hardened by cooling or quenching to martensite. The austenite region (Figure 2) is bounded by a 'gamma loop' which narrows rapidly and closes just within the range of 12%Cr alloys. This austenite region is surrounded by a duplex region of austenite and ferrite (γ+δ). Increasing carbon (and nitrogen) contents widen and extend the duplex region to considerably higher Cr levels, with a relatively smaller expansion of the gamma loop [8, 13].

Alloys cooling through or quenched from the austenitic or duplex region will vary in martensite (or ferrite) with proximity to the austenitic region, and furthermore, as already indicated, any residual microsegregation inherited from solidification will alter the course of local transformations in a weld fusion zone, compared with a HAZ of the same composition.

Not surprisingly, the sensitivity of transformation behaviour to relatively small differences in composition further complicates the prediction and control of HAZ and especially matching weld metal microstructures. To exploit these transformations with minimal additional alloying in order to realise the full economic potential of the leanest 12%Cr alloys is also a significant challenge in composition control for the steelmaker.

Additions are very limited for alloys to be processed easily to a predominantly ferritic condition, while maintaining satisfactory HAZ behaviour. In martensitic alloys there is considerably more scope for alloying, but again this must be limited to maintain practical transformation boundaries for processing and welding. Although carbon is the cheapest and most potent element for controlling transformation, it must also be restricted for optimum weldability and toughness.

4.2.1. Transformation control in 12%Cr ferritics

The early ferritic steels (types 405, 409, 410S) often have compositions placing them outside the gamma loop or at the edge of the duplex region and they may remain essentially ferritic under all cooling conditions. The absence of any transformation leads to rapid and irreversible grain growth in the high temperature HAZ, drastically raising its impact transition temperature and reducing local ductility. Conversely, in simple martensitics (type 410) the hardened HAZ can be improved by tempering to restore reasonable toughness and ductility.

To improve HAZ microstructure control in these and related lean alloys, chromium must be restricted, while in the newer alloys two specific adjustments are applied: carbon is reduced (or almost eliminated by modern steelmaking techniques) and nickel is substituted to promote austenite. Nickel has distinct advantages over carbon: it expands the austenite range (gamma loop) very effectively, but without noticeably increasing the as-quenched hardness of martensite. It is now recognised that a low carbon lath-type martensitic HAZ with less than about 10-20% ferrite offers far better properties than a mixed ferritic-martensitic microstructure [14, 15, 16]. Examples of low carbon lath-type martensitic and mixed ferritic-martensitic HAZ microstructures are shown in Fig. 3. This is achieved in the more recent utility ferritics, with the help of some nickel to obtain the critical balance of composition. The steel itself also gains more strength, ductility and toughness by inheriting grain-refined ferrite due to processing through the austenite range.

Figure 3a) 0.01%C-11%Cr-1.5%Ni (FF = 2.74)
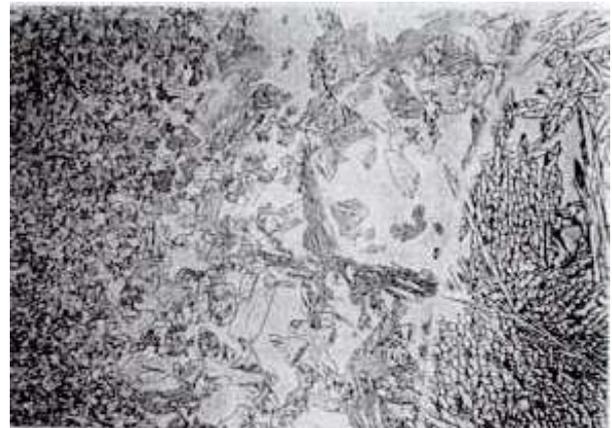 Lath type martensite HAZ   x 500

Figure 3b) 0.02%C-12%Cr-0.5%Ni (FF = 8.42)
 Mixed ferritic-martensitic HAZ   x 500

Predictive equations or diagrams are most convenient for evaluating the behaviour of a given multicomponent alloy or for optimising composition. Two frequently used formulae are the Kaltenhauser ferrite factor [17] and chromium equivalent [18]. These are similar except for some coefficient values, particularly Al, and the number of elements (which are expressed as %):

Ferrite factor, FF = Cr+6Si+8Ti+4Mo+2Al+4Nb-2Mn-4Ni-40(C+N)

Chromium equivalent, Cr_{eq} = Cr+6Si+8Ti+4Mo+12Al+5Nb+1.5W+11V-2Mn-4Ni-2Co-Cu-40C-30N

These formulae provide a parameter against which ferrite-martensite transformation can be assessed. Alternatively, for alloys of around 0.1%C-12%Cr, such as type 410 which is marginally martensitic, the effect on % ferrite of varying individual elements is [7, 19]:

Element	N	C	Ni	Co	Cu	Mn	Si	Mo	Nb	Ti	Cr	V	Al
Change in delta ferrite % per wt% alloying addition	-220	-210	-20	-7	-7	-6	+6	+5	+12 approx	+14 approx	+14	+18	+54

Some applications of the ferrite factor are shown.

In Figure 4 the Kaltenhauser coefficients for elements promoting ferrite and martensite (austenite) are respective co-ordinates for a weld metal constitution diagram recently developed by Balmforth and Lippold [20]. This was derived from the microstructure of argon-remelt buttons and the authors plan improvements using further compositions and a re-assessment of alloy coefficients. Modifications of the Shaeffler diagram such as the Schneider diagram [21] have also been used, and the difference in assumed potency of some alloying elements is obvious.

Figure 4 should be useful for predicting the microstructure of matching weld metal or autogeneous welds in ferritic or lean martensitic stainless steels, but has limitations for predicting HAZ ferrite levels, for which a diagram is being developed with modified alloy coefficients, Figure 5 [22].
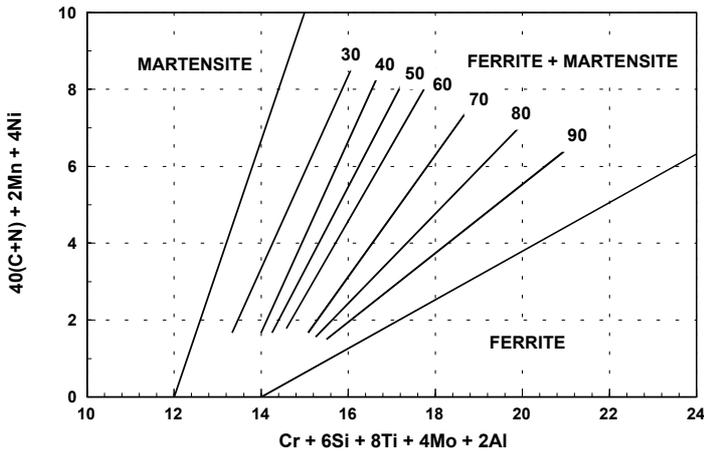

Figure 4: Preliminary ferritic/martensitic stainless steel constitution diagram for low nickel 12-18%Cr weld metals. Iso-ferrite lines are in vol-%. [20]
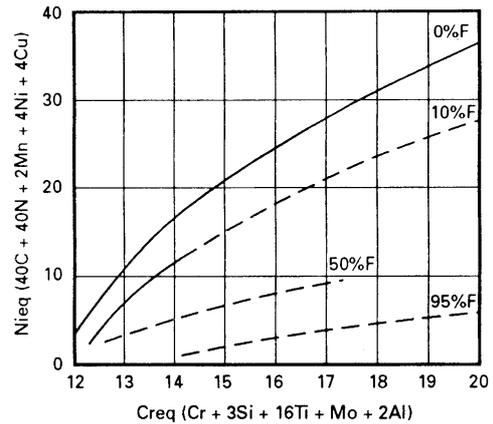
Figure 5: Preliminary constitution diagram for arc weld HAZ's in low carbon 13%Cr steels [22]

Figure 6 shows how the ferrite factor influences the martensite-ferrite transition range for base metal and HAZ [23]. Compared with data for base material, the HAZ transition occurs over a narrower and lower range of ferrite factor, from >90% martensite at FF≤8 to fully ferritic at FF≥12. This effect is owing to diffusion-controlled transformation kinetics effectively contracting the austenite range at fast heating-cooling rates, which is evident from the provisional continuous cooling diagram [15] for a steel of mixed transformation potential, Figure 7.
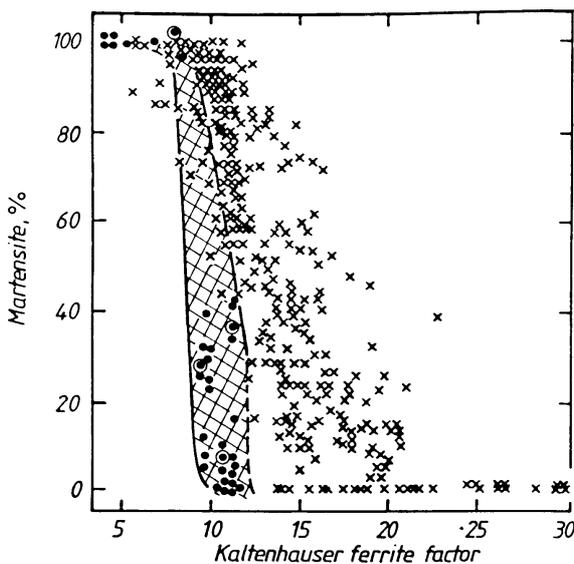

Figure 6: Effect of ferrite factor on structure of 12%Cr ferritic/martensitic steels: x = base metal: hatched area = HAZ data obtained at TWI [23]
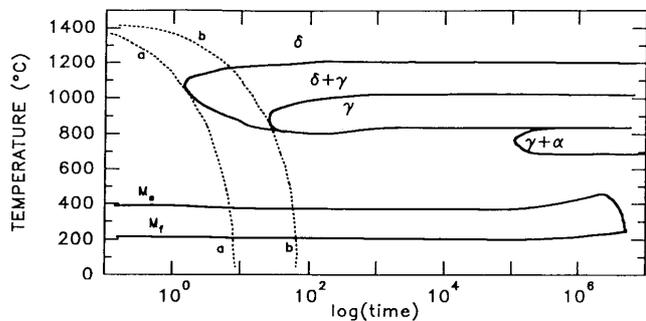
Figure 7: Proposed continuous cooling transformation diagram for the transformation of δ-ferrite to γ in the high temperature heat affected zone during the weld thermal cycle [15].

The drastic effect of excess ferrite on toughness of a mixed martensitic-ferritic HAZ is seen in Figure 8 [16]. This figure is from an early study (1980, Charpy specimens were half-size) using materials with carbon level around 0.06-0.08%, which led to the development of an improved Ni-modified low carbon alloy with better HAZ toughness, similar to the optimised European type 1.4003. However, it should be realised that owing to large differences in peak temperature experienced by various regions of the HAZ, local microstructure and toughness will also vary [15]. The high temperature HAZ and overall engineering properties are the main beneficiaries of composition-transformation control.

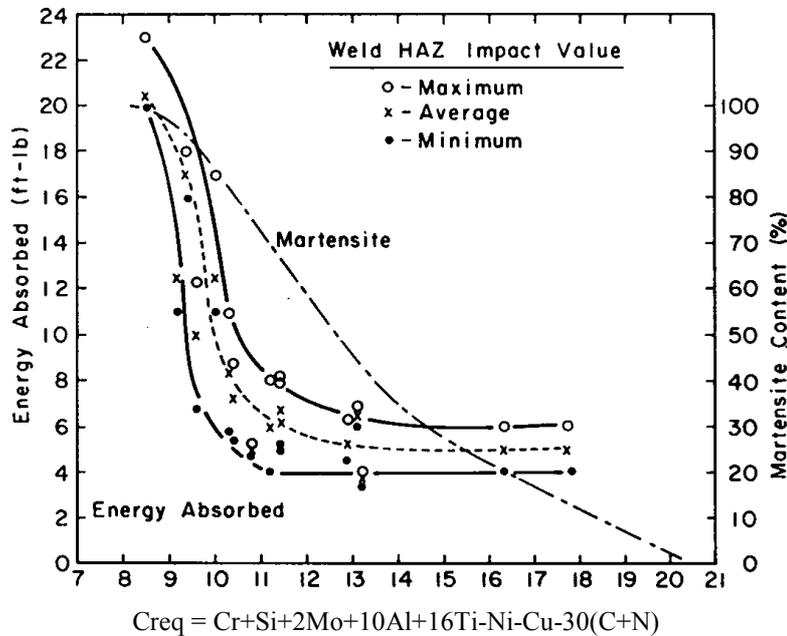$$Creq = Cr+Si+2Mo+10Al+16Ti-Ni-Cu-30(C+N)$$

Figure 8: Effect of chromium equivalent on martensite-ferrite balance and toughness of nickel-bearing 12%Cr stainless steel heat-affected zones at $-29^{\circ}C$ [16].

4.2.2. Sensitisation and the use of strong carbide formers

One remaining question concerns the use of strong carbide formers, as with Ti in alloy 409. The solubility of carbon in 12%Cr ferrite is extremely low and in fully ferritic alloys the HAZ may be sensitised to intergranular corrosion (IGC). In the equilibrium constitution diagrams (Figure 2), only figure 2a with 0.01%C shows that chromium carbide is absent. In type 409, Ti is effective in tying-up carbon and stabilising the HAZ against IGC [24] but a duplex HAZ may be susceptible, with Ti [25] or without [24]. Dual stabilisation of ferritics with Ti + Nb is claimed to be more efficient but as a whole this is not a simple subject, as shown in recent reviews [26, 10].

A fully martensitic HAZ, even with up to 0.15%C as in type 410, is not sensitised to IGC [24], at least in the single pass as welded condition, so martensite's behaviour in a duplex HAZ is more complex. Martensite initially introduces intergranular boundaries highly favourable for carbide precipitation and sensitive to IGC [27]. However, since this martensite increases the effective phase boundary area and will be enriched with carbon (owing to its greater solubility in the prior austenite), less carbon is available for precipitation elsewhere in the microstructure. Carbide precipitation occurs on lath boundaries within martensite, reducing general corrosion resistance but without sensitisation. At a given carbon content, a threshold proportion of martensite is therefore desirable. For a 17%Cr-Ni steel, the following relationship [cited in 27] has been proposed by Miyakusu to suppress IGC, and is perfectly compatible with recent trends in HAZ optimisation of utility ferritics:

$$\%C < (0.0028 \times \%martensite) - 0.013$$

In some early proprietary utility ferritics, Ti was thought to be helpful also to restrict grain growth in the high temperature HAZ, by precipitated Ti(CN) particles. However, this practice has been discontinued in recent alloys such as 1.4003, for at least three reasons: martensite (i.e. austenitic transformation) suppresses grain growth without Ti [15], a predominantly martensitic HAZ is not sensitised, and the use of Ti restricts the scope for alloying to control optimum HAZ microstructure [15].
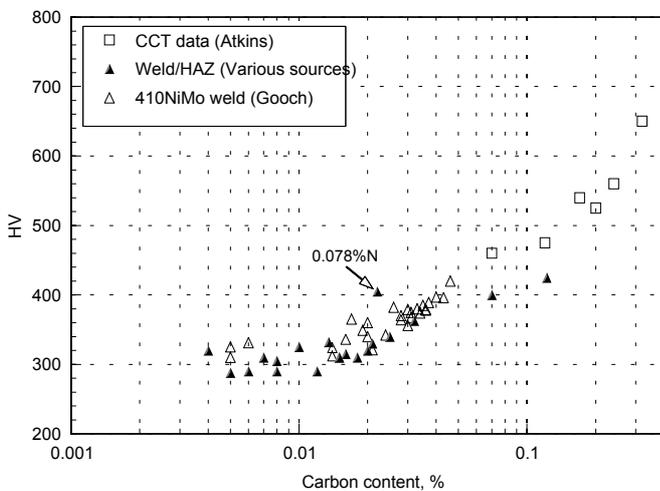
4.2.3. Additional alloying in 12%Cr martensitics

The 12%Cr 'soft' martensitics were first developed as cast alloys in the late 1950's [8] based on the principle of obtaining the essential austenite-martensite transformation by using at least 3%Ni to replace about 0.1% carbon of earlier alloys. The resultant low carbon (<0.05%C) 'soft' lath-type martensite offers an exceptional combination of excellent toughness with high strength and good ductility.

Like the new generation of utility ferritics, they were also developed with the objective of improving both weldability and properties in comparison with previous alloys of their type. In addition, the unique ability of increased nickel to extend good toughness to lower temperatures (unlike carbon) is a particular bonus for the soft martensitics, and this is exploited in alloys with nickel raised to about 6%. Most specifications for soft martensitics include up to 1%Mo, mainly to suppress a tendency to carbide embrittlement when furnace cooling after tempering [28]. This addition also helps to improve corrosion performance.

The new supermartensitics are effectively wrought or forged soft martensitics with further improvements obtained by limiting carbon to around 0.015% or less, and raising corrosion performance with more molybdenum, and also copper in some cases. Up to at least 6%Ni is usually needed to ensure a ferrite-free microstructure. The as-transformed HAZ hardness of these new alloys is close to the theoretical limit for pure carbon-free martensite and, unlike conventional soft martensitics, it is intended that satisfactory service performance can be obtained in weldments without tempering by PWHT.

In Figures 9a and 9b, the effect of carbon on the quenched hardness of predominantly martensitic microstructure is shown for a variety of 12%Cr alloys. This includes the low carbon martensitic HAZ of recently improved utility ferritics, which are grouped with the lean martensitics since this aspect of their behaviour is equivalent. The expanded low carbon region shown in Figure 9b confirms the dominating influence of carbon on quenched hardness, independent of alloy type. However, one particular outlier, the simulated HAZ of an experimental utility ferritic with 0.078% nitrogen shown in both figures, indicates that this element also has an effect, though less than carbon. Some of the new supermartensitics may have a similar nitrogen addition but no welding or HAZ data are yet available for these variants. In soft martensitic weld metals with up to 0.045%N, other workers [29, 30] have been unable to discriminate a noticeable influence of nitrogen on weld hardness in the as-welded or tempered condition, whereas the effect of carbon was clearly evident. In other work on martensitics, nitrogen and carbon similarly raised hardness in plain 12%Cr steels [19], whereas nitrogen had twice the strengthening potency of carbon in 12%CrMoV steels [7].

Figure 9a: Influence of carbon on quenched/HAZ hardness of 12%Cr martensitic steels
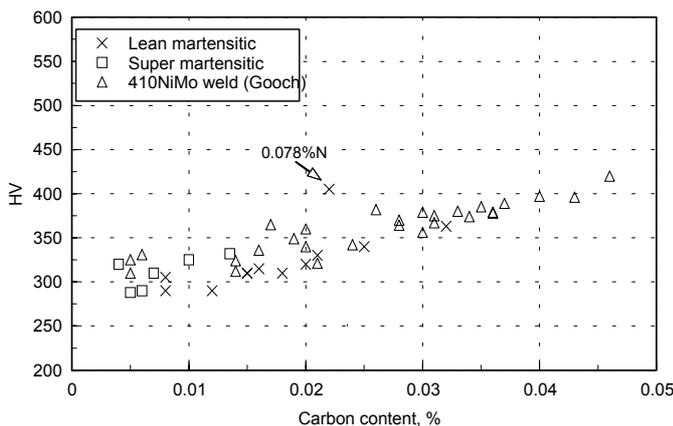

Figure 9b: Influence of carbon on quenched/HAZ hardness of low carbon martensitic steels

4.2.4. Transformation control in low-carbon martensitics

The soft martensitics are air-hardening: cooling rate has almost no influence on the finally transformed martensite, except for small variations in residual austenite and delta ferrite [8]. This well-controlled transformation behaviour confers reliable engineering properties to both base material and matching welds (after heat treatment) in contrast to some of the leaner alloys already described.

The large influence of up to 6%Ni on expansion of the austenite range (γ-loop) is shown for the Fe-Cr system with 0.05%C in Figure 10 [8], which can be compared with the similar region for pure Fe-Cr in Figure 2a-c. Considerable reduction of the lower transformation boundary of austenite (Ac_3) by nickel is noticeable. Figure 11 shows [31] a section of the Fe-Cr system at 13%Cr with nickel up to about 3%. The boundaries of duplex phase are also shown, the lower boundary of which (Ac_1) dictates approximately the maximum temperature of final tempering before significant reversion to unstable austenite occurs.

In practice, a single cycle PWHT (or the second cycle of 2-cycle PWHT) is usually limited to below 620^oC. This fact is occasionally overlooked when 'superior' soft martensitic weld metal is mistakenly chosen to weld a simple martensitic such as type 410, with a typical PWHT required at or above 700^oC (this situation might be accommodated with a second cycle at $<620^oC$).

The close relationship between Ac_1 and tempering temperature for optimum toughness is seen in Figure 12 [28] and also an upward inflection in tensile strength owing to the presence of untempered martensite derived from unstable austenite formed further above Ac_1. The marked toughness peak close to Ac_1 is partly attributed to the formation of extremely fine (optically unresolvable) stabilised austenite at interlath boundaries in the martensite, similar to that in martensitic 18%Ni maraging and 9%Ni cryogenic steels after suitable heat treatment.
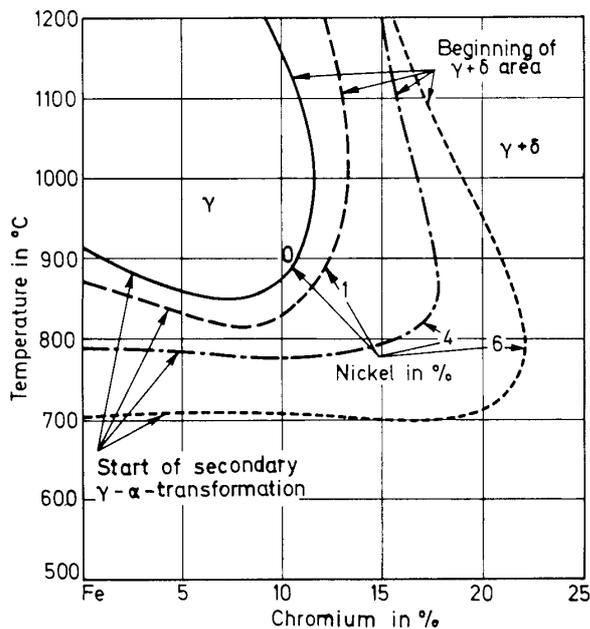

Figure 10: Influence of nickel on the range of γ-phase (austenite) in the iron-chromium system [8]
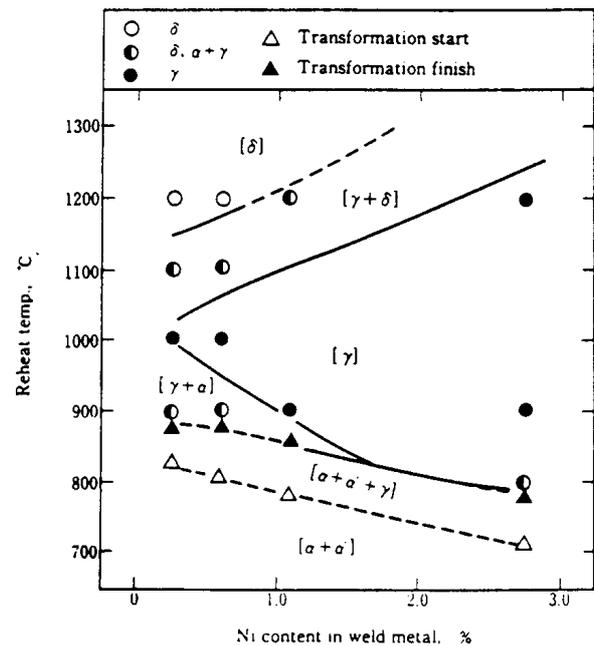
Figure 11: Effect of Ni content on transformation behaviour of 13%Cr weld metal [31]

Two further transformation temperatures concerning austenite and martensite are particularly relevant to welding these alloys. On cooling the Fe-Cr-Ni austenite, transformation is delayed until the martensite start (Ms) temperature is reached and continues over an interval of about 200^oC until transformation is finished (Mf), though 90% transformation is complete about 100^oC below Ms. It is, of course, highly desirable that Mf is above ambient temperature and also that Ms should exceed about 200^oC, to allow some transformation within a practical welding preheat-interpass temperature range. Fortunately these requirements can be met, albeit with little margin.

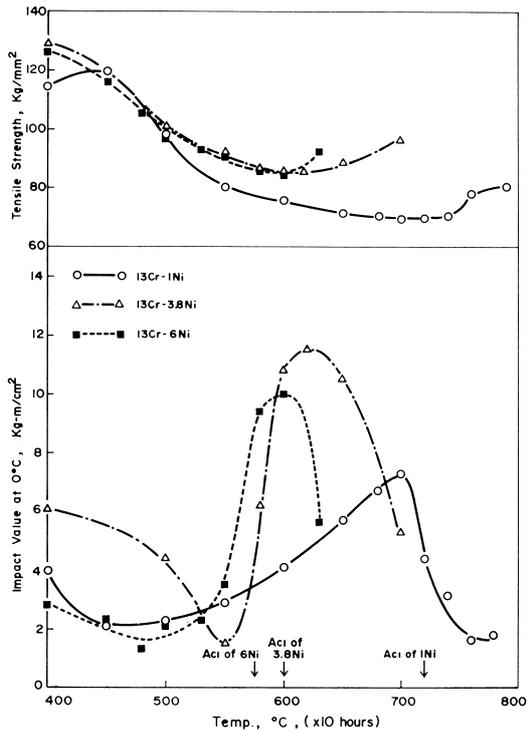Figure 12: Effect of tempering temperature on the mechanical properties of 13%Cr-Ni cast steel [28]
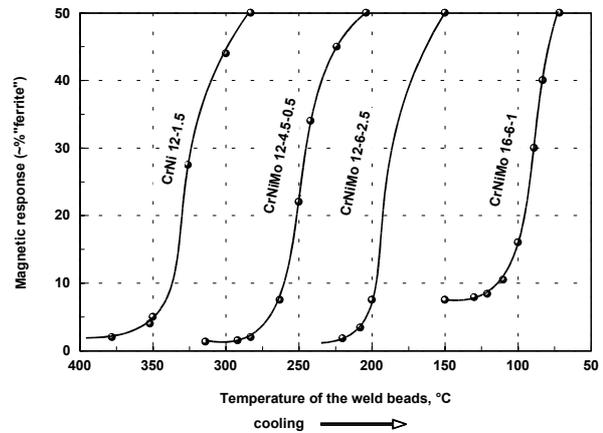

Figure 13: The effect of 1-6%Ni on austenite-martensite transformation, observed by a sharp increase in magnetic response (at Ms) of single weld beads during cooling [32]

Examples of the martensite transformation for four as-deposited weld beads with up to 6%Ni are shown in Figure 13 [32]. Since the cooling austenite is almost non-magnetic, transformation could be measured by magnetic response (as "% ferrite") showing a sharp increase at the Ms. The slight magnetic response of the austenite prior to Ms indicates the level of residual ferrite present, which varies with nickel content. Residual austenite was also found to rise from 2% to 9% as nickel increased [8].

As with the leaner alloys, equations and constitution diagrams have been developed for assessing quantitatively the influence of alloying elements on the transformation temperatures important for processing and the optimum microstructure.

The reported influence of a number of elements on the Ac_1 and Ms transformation temperatures are given [7,19] as follows:

Element	C	Si	Mn	Cr	Ni	Mo	Al	Co	V	W
Change in Ms, OC per 1% element	-474	-11	-33	-17	-17	-21	-	+ (slight)	-	-11
Change of Ac1, OC per 1% element	-	+25	-25	-	-30	+25	+30	-5	+50	-

The following formula, derived from alloys with 10-18%Cr and 0.7%Ni, has been recommended [22,33] to predict Ms temperature with satisfactory precision:

$$Ms\ (^{\circ}C) = 540 – (497C + 6.3Mn + 36.3Ni + 10.8Cr + 46.6Mo)$$

For guidance on estimating the Ac_1 temperature of low carbon highly alloyed 13%Cr steels, the following formula has recently been presented [22]:

$$Ac_1(^{\circ}C) = 850 – 1500\ (C+N) – 50Ni – 25Mn + 25Si + 25Mo + 20(Cr-10)$$

For 17%Cr steels, the following also indicates the relative influence of elements additional to those already given [27]:

$$Ac_1\ (^{\circ}C) = 310+35Cr+60Mo+73Si+170Nb+290V+620Ti+750Al +1400B$$

$$– (250C+280N+115Ni+66Mn+18Cu).$$

Owing to the slower diffusion and transformation kinetics around Ac_1, and the competitive influence of many elements, its effective temperature is not so well defined as the Ms, which is essentially a diffusionless transformation. As a generalisation, Ac_1 temperature is lowered by elements known to be austenite formers, and raised by ferrite formers, whereas Ms temperature is lowered by the total alloying level. However, owing to local inhomogeneities, the residual transformations around Mf also become less predictable.

The transformed microstructure of these alloys can also be assessed on a constitution diagram such as the Schaeffler or a modified Schaeffler diagram. The higher level of alloying probably makes this approach more reliable than methods based on the ferrite factor determined on much leaner alloys. Figure 13 shows an expanded portion of the Schaeffler diagram including the location of some relevant alloys [8].
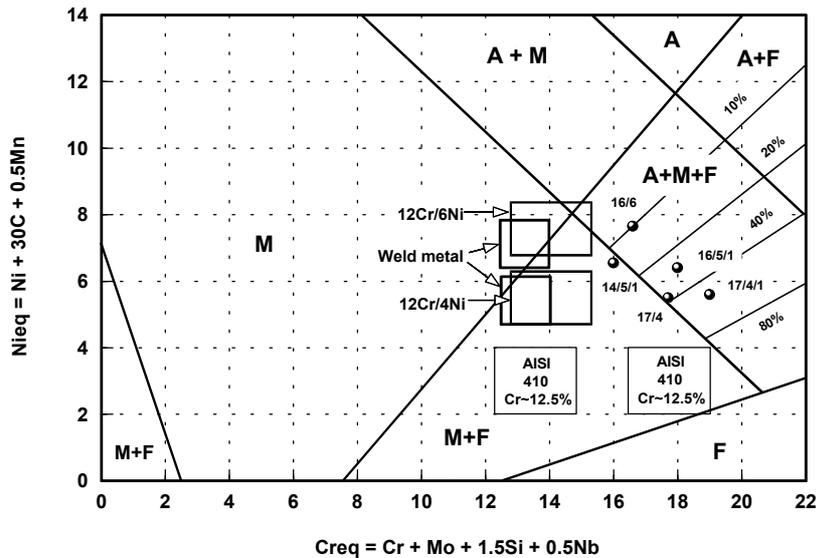
Figure 14: Location of stainless chromium steels and low carbon martensitic chromium-nickel steels and weld metals on a section of the Schaeffler diagram [8]

This gives a satisfactory indication of the relative levels of residual ferrite for the two soft martensitics discussed earlier. The values for the Schaeffler Cr and Ni equivalents are inevitably an approximation for these alloys. The diagram would also place a typical supermartensitic just within the martensite + ferrite region, close to the 12%Cr – 6%Ni alloy shown on Figure 14.

More recently, Karlsson et al [11] have developed a constitution diagram to accommodate supermartensitic weld metals (Figure 15), based on extending Balmforth and Lippold's diagram shown in Figure 4.

Figure 15: Constitution diagram for supermartensitic weld metals (from ref 11).

5. UTILITY FERRITICS

Table 1:   Plain 11-12%Cr – low C < 0.03% - little additional alloying

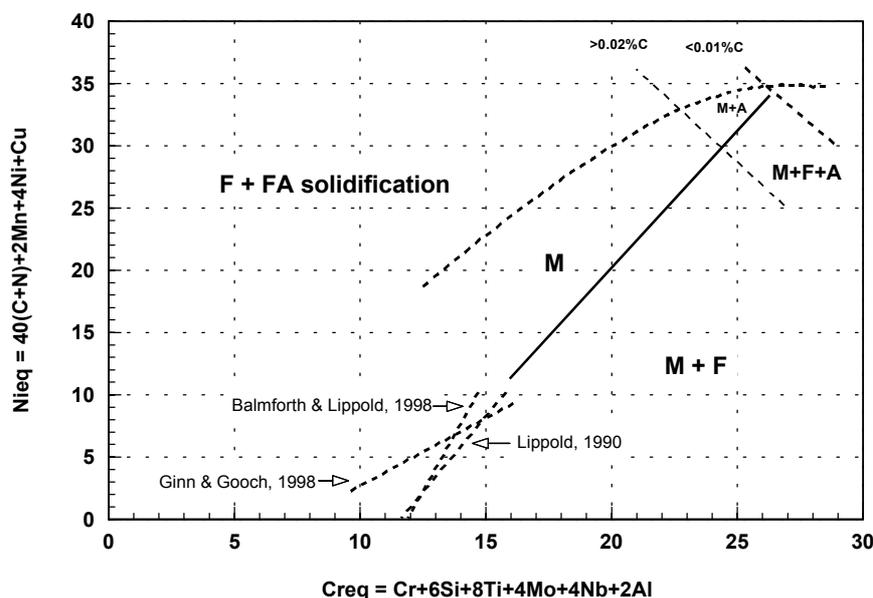| GRADE/ TRADENAME	Typical composition, weight %							Manufacturer
	C	Mn	Si	Cr	Ni	N	Others	
405	0.025	<1	0.5	12	-	-	Al 0.2	Generic
409	0.025	<1	0.5	11	-	-	Ti 0.2	Generic
410S	<0.08	0.5	0.3	12	<0.5	-	-	Generic. API 5LC52-1200 pipe
3CR12	0.025	1.2	0.5	11.5	0.5	0.02	-	Columbus steel [34]
Nirosta 4003	0.02	1.1	0.5	11	0.4	-	-	Krupp [35]
CR13LC	0.03	1.5	<0.3	13	0.2	<0.03	Nb 0.035	Mannesmann. Pipe (25% ferrite). [36, 37]
LC-12Cr	0.03	0.8	0.4	12	0.4	-	-	Kawasaki
Polarit 850	0.02	1.1	0.4	11	0.8	<0.02		Outukumpu Polarit Oy [14, 38, 39, 40]

5.1 Microstructure

These corrosion resistant 12%Cr steels have been developed with very low carbon contents and close control of the martensite/ferrite balance. Some of the steels are ferritic, but the more modern versions have a dual phase structure which consists of fine grained low carbon martensite and fine grained ferrite, which is achieved by direct controlled cooling from the hot rolled material – usually sheet or plate. Representative microstructures of materials with high and low ferrite factors are shown in Fig. 16. The microstructures are balanced for ease of forming and fabrication, and to avoid the extremes of properties and welding behaviour usually associated with fully ferritic or martensitic structures.
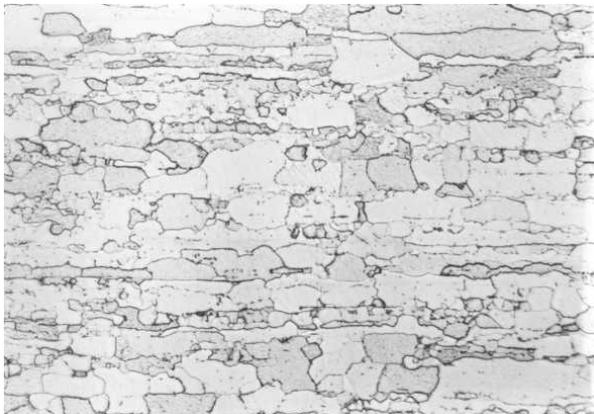
Figure 16 a) First generation microstructure
FF >9   x400
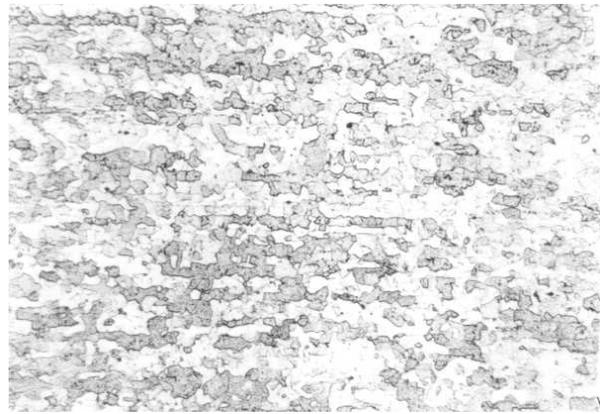
Figure 16 b) Second generation microstructure
FF = 7.8   x400

5.2 Mechanical properties

The basic mechanical properties of the various grades are dependent upon carbon content, alloy content and microstructure, but generally fall within the ranges shown below. The older fully ferritic grades are typically at the lower end of the strength range, whilst the dual phase steels can be balanced and processed to give higher strength levels.

0.2% Proof Stress: 320 – 400 MPa

Tensile Strength: 450 – 650 MPa

Elongation: 20 – 30%

Toughness:	Impact values of parent steels are typically in excess of 100J at +20°C with some grades giving values as high as 200J. Ductile/brittle transition temperatures are typically in the range -20°C to -40°C and most grades give poor lower shelf values at temperatures below -50°C. In this respect these steels are not intended for low temperature or cryogenic service.

The best combination of mechanical properties is achieved with thinner materials. Loss of tensile properties (~10%) can be expected above 6mm and loss of toughness above 12 – 15mm thickness.

5.2.1 Elevated temperature properties

Although not primarily designed as high temperature materials, this group of steels offers useful properties up to moderate temperature. The maximum service temperatures range from 450°C for continuous temperature/loaded structures up to about 750°C for intermittent temperature/unloaded structures. The 12%Cr content provides good scaling and oxidation resistance as well as useful performance in sulphur-bearing and hot industrial gases/fumes. In addition, the newer steels do not show significant "475°C" embrittlement in the range 370-510°C. Experience with the older steels is also satisfactory, although high Cr+Ti have been implicated in the brittle failure of a deviant ferritic steel with 13.4%Cr-0.5%Ti [Creamer, 1980].

5.3 Product forms

The modern dual phase types are produced as cold rolled strip and sheet up to 3mm and hot rolled coil and plate up to about 25mm in thickness. Other manufactured forms include seamless pipes and tubes, cold formed sections, perforated plate and expanded metal. The older, plain ferritic types are usually restricted to 6 mm in thickness.

5.4 Applications

Sugar refining plant; hoppers, chutes and silos in the metal and minerals handling and processing industries; vehicle/rail car bodies/chassis; fertiliser and refuse slurry handling plant; high temperature exhaust ducts and flues.

In general terms the steels provide properties which bridge the gap between coated/painted/galvanised steels and the more expensive standard austenitic stainless steels. Although much softer than low alloy Q+T steels, they may be more cost-effective in applications requiring wet abrasion resistance.

5.5 Welding and weldability

These steels are routinely welded without preheat using most of the common arc welding processes and austenitic stainless steel consumables. These provide adequately strong and tough weld metal, minimise the risk of HAZ hydrogen cracking and are sufficiently highly alloyed to cope with dilution of the parent steel(s).

5.5.1 Welding consumables

The readily available type 309L consumables are most commonly used, and are considered to provide superior tolerance to dilution with base material, compared with types 308, 308L and 316L. Dilution leading to a 'triplex' austenitic-ferritic-martensitic weld metal microstructure may give poor ductility and toughness [41]. Type 309L consumables are also suitable for dissimilar welds between utility ferritics and most other grades of C/Mn and stainless steels. For applications such as hot exhaust ducting operating up to 600°C weld metals with better thermal stability are preferable, such as type 309 with controlled ferrite and ~0.06%C or one of the leaner nickel-base filler metals which offer a better match of thermal expansion, albeit at higher cost.

Welds are rarely subjected to PWHT, but when specified (possibly with the intention of improving fatigue life) this should be at around 620°C for a limited period and its effect on the weld metal must be considered – Ni base weld metal may be an option. For type 409 steels used in automotive exhaust

systems, matching composition gas shielded metal cored or self shielded flux cored and similar 409Nb solid gas shielded welding wires are used.

5.5.2 HAZ properties

Because of the use of non-matching weld metals, the overall properties of weldments in utility ferritics have until recently been dominated by the HAZ, particularly ductility and toughness. A low carbon, martensitic HAZ with minimal ferrite is now considered optimum and the compositional factors controlling this are determined by steelmaking and grade limitations. The modern proprietary grades are now balanced to offer improved HAZ properties. However, the older grades, e.g. types 405, 409 and 410S, are likely to have HAZs with poor toughness and may not be fracture-safe except in thin sections. Even with the modern grades, most manufacturers' literature considers it prudent to limit welding heat input and interpass temperature and so restrict grain growth in the HAZ. Typical suggested limits are 1kJ/mm heat input and 100°C maximum interpass temperature and, if strictly adhered to, these would severely limit the use of higher productivity welding processes such as the flux cored and submerged arc processes. In real terms significant improvements in ferritic HAZ toughness arising from limiting grain size can only be achieved at heat inputs as low as 0.1 – 0.2kJ/mm [42].

Studies on actual and simulated HAZs generally show ductile/brittle transition temperatures (DBTT) above 0°C and for this reason it is generally recognised that these steels should not be used for critical welded fabrications which are pressure containing or similarly loaded.

However, toughness of the HAZ is critically dependent upon whether it consists of grain coarsened ferrite or low carbon tempered martensite. The latter is much tougher and is the basis of the claim made by certain producers that their steels give enhanced HAZ properties [40, 35]. There is, however, a fine dividing line between the two microstructures and very careful control of composition is required to achieve the optimum properties (Fig. 7). For this reason it is possible to obtain significantly different properties from different casts of nominally the same grade of steel [16].

5.6 Structural integrity

In spite of the HAZ toughness limitations, these steels have been used in a wide range of welded fabrications with few, if any, reported instances of brittle fracture. The reasons for this are:

a) The potential loss of toughness is well recognised and the most commonly used thicknesses are below 10mm and often below 6mm, which results in an effective reduction of the DBTT.

b) Normal welded joints seldom have weld fusion lines which result in a through thickness planar HAZ, so any crack initiating in the embrittled HAZ is likely to be arrested in either tough parent steel or austenitic weld metal.

Many practical fabrication guidance notes recommend that planar HAZs are avoided, either by modification of the weld preparation, or by ensuring good penetration of individual weld beads to give an irregular fusion line/HAZ.

c) With the correct choice of consumable, the risk of either hydrogen or solidification cracking (which could be an initiating defect) is low. However, precautions should be taken to avoid the risk of fatigue cracking in service.

Although these steels tend not to be used in pressure containing structures, they are often exploited in other safety critical structures, particularly road and rail vehicles. For these structural applications, special tests have been developed which are designed to test models or actual welded components under simulated accident conditions. They examine load absorption and deformation as well as the failure mechanism [43].

5.7   Corrosion resistance

These steels with 11 to 13%Cr are just "stainless" but are not designed to compete directly with 300 series austenitic, duplex or higher alloyed stainless steels in more aggressive media. Even under atmospheric conditions, particularly marine, urban and industrial, they will exhibit some staining and discolouration, and are therefore not suitable for external decorative or industrial applications. The dispersed martensite often present in the more recently developed types may also be susceptible to preferential attack in some test media [41].

5.7.1   Pitting corrosion

The utility ferritics are not designed for use in pitting environments and, to avoid pitting in an aqueous environment at room temperature, the chloride content should not exceed 200 ppm [44]. The PRE_N[***] values are very low at ~12 when compared with type 316L stainless (PRE_N ~24) and 22%Cr duplex stainless steels (PRE_N 33 -35).

5.7.2   Sour service

Somewhat surprisingly, type 405 stainless is listed in NACE MR 0175-95 as being acceptable for direct exposure to sour environments provided the steel and, presumably, the weld/HAZ do not exceed 22HRC maximum hardness.

5.7.3   Intergranular corrosion

The sensitivity of the utility ferritics to HAZ intergranular corrosion depends critically upon the microstructure of the HAZ [24]. Type 409 with a ferritic HAZ plus titanium stabilisation, and type 410 with a fully martensitic HAZ, were not sensitised, whereas type 405 with a duplex martensite-ferrite microstructure was found to be sensitive to intergranular corrosion – albeit in media that are less aggressive than those used in the recommended practices for austenitic stainless steels.

5.7.4   Corrosion/abrasion

Under dry abrasion conditions (moisture up to 4%) utility ferritics offer no advantage over mild steels. At higher moisture levels they are greatly superior to all non or low alloyed steels and comparable to 304L and 316L types.

A further benefit lies in so-called "slideability", the ease with which materials, powders, minerals, etc., move in chutes, silos and hoppers. In this respect they show advantages over all plain mild, coated and galvanised steels and even some 300 type stainless steels and aluminium alloys [44].

5.7.5   High temperature corrosion (see also 5.2.1)

The utility ferritics offer scaling resistance in dry air up to about 800°C but will suffer severe corrosion if temperatures fall below the dew point and acids form from combustion products. Under such conditions they offer little benefit over mild steel.

[***] Pitting resistance equivalent number, $PRE_N = Cr + 3.3Mo + 16N$

6. LEAN MARTENSITICS

Table 2:   Plain 11-13%Cr steels with various C contents, low nickel

GRADE/ TRADE NAME	Typical composition, weight %									Manufacturer Notes
	C	Mn	Si	Cr	Ni	Mo	Cu	N	Others	
410	<0.15	0.5	0.3	12	<0.5	-	-	-	-	DIN X10Cr13. CA15 (cast)
414	<0.15	<1	0.5	12.5	1.8	-	-	-	-	-
420	0.2	0.5	0.3	13	0.2	-	-	-	-	API 5CT L-80 (tube)
'KCR-13A'	<0.08	<1	<0.5	12	<1	<0.6	-	-	-	Kubota. Centricast tube [45]
CR13LC (+Ni)	0.02	1.5	0.2	13	1.5	<0.1	0.5	<0.03	-	[37, 36] Mannesman (<1% ferrite) Pipe
'12Cr-mod'	0.01	1.5	0.2	11	0.8	-	0.5	<0.02	-	[46, 47, 48] Kawasaki. Pipe

6.1   Microstructure

These steels contain 11-13% chromium with minimal additional alloying. The older standard grades 410, 420, etc., have carbon contents in the range 0.1 to 0.2%, are air hardening and give a predominantly martensitic microstructure. The steels are invariably heat treated before use, and all grades contain tempered martensite with varying levels of chromium carbide and residual ferrite. The more modern lower carbon grades have small alloying additions and are "tuned" to avoid the presence of ferrite and so minimise HAZ grain coarsening during welding. These represent an evolutionary step towards the new 'lean supermartensitic' steels (see Table 4-1).

6.2   Mechanical properties

6.2.1 Room temperature

The mechanical properties of the various grades vary depending upon product form, carbon content and heat treatment, but can be divided into two sub-groups:

i)   Higher carbon grades (type 410/420)

0.2% Proof Stress:	500 – 1000 MPa
Tensile Strength:	700 – 1400 MPa
Elongation:	15 – 30%
Toughness:	Impact values are modest and generally less than 50J at room temperature: the highest carbon grades (up to 0.3%) can be heat treated to give proof stresses in excess of 1100 MPa, but with correspondingly low ductility and toughness. At the highest strength levels these are reduced to virtually zero, and such grades have very limited applications.

ii)   Lower carbon grades (KCR-13A, etc.)

0.2% Proof Stress:	400 – 700 MPa
Tensile Strength:	600 – 800 MPa
Elongation:	20 – 35%
Toughness:	These lower C steels with modest alloying derive their properties from tempered low carbon martensite and achieve good combinations of strength and toughness, e.g. 150-250J at $+20^{\mathrm{O}}$C. They also exhibit useful sub-zero values at -40°C but retain little useful toughness below -75°C.

6.2.2 Elevated temperatures

Type 410/420 alloys retain reasonable high temperature properties and at 600°C exhibit about 45% of the room temperature strength. For use at temperatures up to 500°C, the steels are tempered at 600°C and any subsequent service embrittlement in the critical $350\text{-}500^{\mathrm{O}}$C range is minimal. Note, however, that these alloys are reported to be susceptible to phosphorus-dependent reversible temper embrittlement [49].

The lower carbon steels are not specifically designed for elevated temperature use, but may find application for flowlines containing hot oil at temperatures in the range $100\text{-}200^{\mathrm{O}}$C. These grades show minimal loss of proof stress up to about 400°C, followed by a fairly steep decline. As with all 12%Cr lean martensitic steels, there is evidence of some loss of ductility in the $350\text{-}500^{\mathrm{O}}$C range.

6.3   Product forms

Castings, forgings and plate.

Seamless, centricast and welded tubes (lower carbon grades).

6.4   Applications

Most applications are designed to exploit one or more of the following features:

ii)   basic stainlessness (12%Cr)

iii)   modest cost

iv)   high strength

v)   elevated temperature properties.

They include: hydrocrackers, reactor vessels, distillation plant and associated pipework in oil refineries:

furnace parts, linings and run out rolls in the steel industry:

cast steam valve bodies, pumps, shafts, turbine parts and burner nozzles where modest corrosion resistance or high temperature properties are required.

downhole tubulars; with the lower carbon grades also being promoted for flow lines and linepipe in the oil and gas industry.

6.5   Welding and weldability

6.5.1 Higher carbon versions (C >0.1%)

These steels (typified by type 410, with 0.08-0.15%C) are usually welded with "matching" 12%Cr consumables, particularly where similar mechanical properties are required of the weld. In such cases, the completed weldment must be subject to PWHT to achieve reasonable toughness and ductility in both the HAZ and weld metal. Until PWHT there is a risk of hydrogen induced cracking in the HAZ or the weld metal or both and an example of weld metal hydrogen cracking is shown in Figure 17. To avoid hydrogen cracking, preheats of between 200°C and 300°C and low hydrogen consumables/processes should be

used. It is particularly important that flux covered electrodes and fluxes for submerged arc welding are used in the redried/rebaked condition as recommended by the manufacturer. In addition, the interpass temperature should not fall below the preheating temperature.

Figure 17: Typical hydrogen crack in martensitic weld metal – note presence of some light etching δ-ferrite. x300

Although high preheats (200-300°C) are generally recommended, it may be possible to reduce the preheat temperature to 100°C or lower if thinner components with less restraint are being welded with a very low hydrogen potential process, e.g. GTAW welding with clean wires.

Mechanical properties of the weld metal are, like the parent steel, highly dependent upon PWHT. In the as-welded condition toughness and ductility are virtually zero and care should be taken to avoid thermal or physical shock before the component is heat treated. (Weldments in the highest carbon types should also be kept dry – see below.) A typical PWHT would be a very slow cool to room temperature to allow the full martensite transformation to take place (range is Ms – 350°C: Mf – 100°C), then temper at 680-720°C, followed by air cool. To ensure lower hardness values (e.g. <22HRc for NACE) and better toughness, PWHT at 745°C is preferred. This PWHT will give impact values of about 35 – 40J at +20°C which is comparable with the parent steel.

Specifications for consumables directly matching type 410 have limited scope for eliminating the embrittling effect of retained ferrite, and in cases where such welds are required with improved toughness, then weld metal modified with about 1.5%Ni can be used. For single tempered welds optimum weld metal properties are obtained after PWHT at about 700°C. This is closer to the Ac$_1$ temperature (~750°C) for this composition which is reduced by the addition of nickel when compared with that of the plain 410 steel (Ac$_1$ ~ 800°C). PWHT times can be extended, but higher temperatures may cause re-hardening with fresh martensite formation on coolout. A wide range of improved properties can be achieved with a double PWHT. This is essential for NACE conformance in sour service (<22HRC), and it is necessary to cool to ambient temperature between each cycle.

There may be situations where a PWHT is not practicable (e.g. repair of a large assembled component) and a non-matching austenitic filler must be used. The options available are similar to those for the utility ferritic steels, namely 308L, 316L, 309L and 307 types. The last two types are generally preferred because of their higher strength, comparable to type 410 steel, and their ability to accommodate dilution. The austenite content of the weld metal will hold any hydrogen in solution, and should prevent hydrogen cracking in the HAZ. However, it must be recognised that the HAZ will be largely untempered, will have poor ductility/toughness, and in restrained conditions may still be liable to crack.