The highest carbon grade, type 420, is rarely welded[#], possibly because of its reputation for poor weldability, even though the related creep resistant 12%CrMoV is successfully welded with matching consumables. In this case, a preheat-interpass range of 250-350^{O}C is used (Ms ~290^{O}C), which allows some transformation, tempering and hydrogen diffusion in multipass weldments. Strict precautions are taken to avoid cold cracking prior to PWHT: ideally, welds are slowly cooled to around 100-150^{O}C to ensure full transformation and then directly given PWHT (at 760^{O}C/1 – 4h in this case). If welds must be cooled to ambient, the transformation step is followed by reheating at 350^{O}C to promote hydrogen release before coolout. Prior to PWHT, weldments must be kept completely dry because exposure of highly hardened (~550HV) HAZs and weld metal to moisture can provoke stress-corrosion cracking. The possibility that some surface residues may be hygroscopic, particularly condensed welding fume, should not be overlooked.

6.5.2 Lower carbon versions (<0.1%C)

Welding developments have been largely confined to the GTAW, GMAW and SMAW processes and the majority of applications have concentrated on the circumferential butt welding of pipes for flow lines, etc. A number of different consumable options have been explored:

a) matching composition using preheat and PWHT – a similar approach to that adopted for the higher carbon grades [45]

b) matching composition without preheat or PWHT [46] – this appears to have been an experimental exercise which was not pursued in later trials

c) weld metal of the low carbon soft martensitic type, e.g. ER410NiMo [37]. If this approach is adopted, care must be taken to choose a PWHT procedure which is appropriate to the weld metal which will have a reduced Ac_1 temperature when compared with the parent steel (see Section 7 - ‘soft martensitics’).

d) duplex or superduplex weld metals usually without preheat or PWHT [37]. This approach is similar to that adopted for the supermartensitic stainless steels (see Section 8).

With the possible exception of (b), all above options provide weldments with more than adequate tensile properties, and cross weld tensile specimens tending to fail in the base material. They also give reasonable impact toughness in both weld metal and HAZ. However, values quoted for HAZ properties may be artificially high because specimens tended to sample not only the HAZ but also significant proportions of tough parent steel.

6.6 Corrosion resistance

Type 410 and 420 alloys have a long application history where modest corrosion resistance, some cavitation resistance and high temperature properties are required at moderate cost. More recently work has been carried out to explore a wider range of applications in the offshore oil and gas industries.

6.6.1 CO_2 and NaCl service

The lower carbon versions are promoted primarily for offshore flowlines operating under wet CO_2 conditions. They offer significant benefits over mild steels which require the use of inhibitors, which in turn become less efficient at high temperatures. These steels are suitable for service up to about 200^{O}C.

The reduced carbon content combined with modest additions of nickel up to about 1.5% and copper to about 0.5% have a significant effect in reducing corrosion rate in solutions with 20%NaCl and 3MPa CO_2. A corrosion index based on %Cr -10%C + 2%Ni has been proposed [46] but, surprisingly, this does not include a factor for copper, even though it would appear to have an effect equal to that of nickel. Copper also acts as a strengthening element and is used at the 0.5% level to ensure a minimum yield strength of 550 MPa (80ksi) [46].

[#] Weld metals based on various modifications to alloy 420 are used extensively for cladding concast steel mill rolls, using the submerged arc process and tubular wires.

6.6.2 Sour service

Some testing has been carried out under simulated sour conditions, but even small levels of H_2S (>0.01 bar) have lead to high corrosion rates and sulphide-induced stress corrosion cracking (SSC) [37].

Type 410 (not 420) and cast alloys CA15/CA15M are included in NACE MR0175, which notes that they may exhibit threshold stress levels (according to NACE TM0177 testing) lower than those for other materials in the standard. A 3-stage heat treatment including solution treatment is invoked for base material, which must meet <22HRC hardness levels, as must welds.

7. SOFT MARTENSITICS

Table 3: Low carbon 13-15%Cr steels with 4-6%Ni up to 1.5%Mo

GRADE/ TRADE NAME	Composition, weight %								Notes
	C	Mn	Si	Cr	Ni	Mo	Cu	Others	
13Cr-4Ni	0.04	0.5	0.3	13	4	0.4	-	-	DIN G-X5CrNi 13 4 (cast) CA 6NM (cast) F6NM (forged)
13Cr-6Ni	0.04	0.5	0.3	12.5	5.7	0.5	-	-	DIN G-X5CrNi 13 6 (cast)
ZGOCr13Ni6Mo	0.06	0.7	0.8	13	5.8	0.6	-	-	China
00Cr13Ni5MoNb(Ti)	0.02	0.1	0.2	14	6.6	1.3	-	0.5Nb + Ti	China
16Cr-5Ni-1.5Mo	0.04	0.5	0.3	16	5	1.5	-	-	DIN X4CrNiMo 16 5 DIN G-X5CrNiMo 16 5 (cast)

7.1 Microstructure

These steels are a development of the plain 12%Cr steels in that they have a lower carbon content, with additions of 4 - 6% nickel and 0.5 – 1.5%Mo. The steels are always supplied in the tempered condition, and the microstructure consists of a fine lath martensite with little or no residual ferrite. A very fine dispersion of stable austenite is formed during heat treatment and this contributes to the relatively high toughness of these alloys.

7.2 Mechanical properties

7.2.1 Room temperature

Properties of the various grades are dependent upon composition and heat treatment, but are typically in the range:

0.2% Proof Stress: 620 – 800 MPa

Tensile Strength: 800 – 950 MPa

Elongation: 15 – 25%

Toughness: Cast alloys have good toughness down to at least –50^{O}C with typical values in the range 60 – 80J. Useful values 25 – 35J can be obtained at –100OC. Forged versions usually have somewhat better toughness than the cast alloys.

7.2.1 Elevated temperature

These alloys were not primarily designed for high temperature use which is limited by their relatively low Ac_1 temperature. Nevertheless, they retain more than 80% of their yield and tensile strengths at temperatures up to $400^{O}C$, followed by a fairly steep decline at higher temperatures. As with most of the 12%Cr steels, they also show a modest ductility dip at about $400^{O}C$ [50].

7.3 Product forms

Castings, forgings, seamless tubes.

7.4 Applications

The alloys have good general corrosion resistance and some resistance to stress corrosion cracking in CO_2 and H_2S environments. They are also particularly resistant to wet abrasion and cavitation and therefore find widespread application in the following areas:

heavy section water turbine components, including runners, impellors, diaphragms, diffusers, impulse wheels, propellers, etc.:

pump and valve bodies for the power generation and petrochemical industries.

wellhead equipment for the offshore oil and gas industries.

7.5 Welding and weldability

Welding is readily carried out using matching low carbon consumables (usually 0.04%C, though specifications allow <0.06%C) and the more commonly used arc welding processes. The weldability of these grades is improved relative to that of the plain 12%Cr steels because of the formation of tough low carbon martensite in both the weld metal and HAZ, which reduces hydrogen cracking sensitivity, and the low delta ferrite content which reduces the tendency to grain growth. In spite of these features, it is still necessary to take precautions to avoid hydrogen cracking in both the HAZ and weld metal. Consumables must be selected and/or conditioned to give weld metal hydrogen levels of less than 5ml/100g of weld metal. Preheating is also essential on thicker (>20mm) and more highly restrained structures, the optimum preheat-interpass temperature range of $100\text{-}200^{O}C$ being within the martensite transformation temperature range ($\sim 100\text{-}250^{O}C$). Interpass temperatures above the Ms lead to coarse columnar dendritic microstructures with inferior properties after transformation.

For minor or non-critical welds, and to avoid PWHT (where some HAZ hardening is acceptable in service), it is possible to use an austenitic consumable, 308L or 309L type. These will give reasonable weld metal properties and the high solubility of any hydrogen in these weld metals will avoid the risk of any HAZ cracking without preheat. A similar procedure using duplex or superduplex consumables will provide increased strength. For in-situ repairs/overlays, matching consumables are occasionally used without PWHT, although limited ductility and toughness should be recognised. A low interpass temperature range of $100\text{-}150^{O}C$ is recommended [8] to ensure that each bead transforms to martensite which can be partially tempered during the deposition of subsequent weld passes. The final pass(es) experience less reheating and will be harder, with lower ductility.

For the majority of welded applications, repair of castings, joining of forgings, etc., a PWHT is invariably carried out, usually in the range $580\text{-}620^{O}C$. Minimum hardness values are achieved following heat treatment at $600^{O}C$ for 20h or $620^{O}C$ for 10h, although satisfactory ductility and toughness are obtained at much shorter durations. Prolonged heat treatments are generally applied to very large thick-walled castings and it is important to cool down to below $100^{O}C$ after welding to allow for full transformation to martensite. However, complete cooling to ambient temperature before PWHT should be avoided for very thick components, to avoid the risk of cold cracking.

If hardness levels in 13%Cr-4%Ni welds are restricted, e.g. by NACE MR 0175 (<23HRC), then a double tempering treatment is required in combination with low carbon levels (<0.035%). Common practice is $675^{O}C$/10h plus $605^{O}C$/10h with an intermediate air cool to ambient temperature. More recent work [29] indicates that $650^{O}C + 620^{O}C$ is an optimum condition with intermediate cooling to ambient or even $0^{O}C$ to ensure as complete a martensite transformation as possible. It should be noted that these PWHT temperatures are just within the limits specified by NACE MR0175.

An important practical issue concerns the fact that weldment hardness surveys are normally conducted using the Vickers method with low indentation load, and the HV values then converted to HRC by reference to standard tables such as ASTM E140. However, it is now firmly established that the ASTM HV-HRC conversion (23HRC = 254HV) is incorrect for such welds, and a conversion of 23HRC = 275HV should be used [29].

Weld metal hardness values below 23HRC can be achieved with a single heat treatment of sufficient duration below $620^{O}C$, provided the carbon content is controlled to extremely low values of less than 0.01%. The effect of carbon content is clearly shown in Figure 18 [29], where re-hardening occurs with higher carbon and longer duration, probably caused by destabilisation of initially stable austenite formed around the Ac_1 temperature.

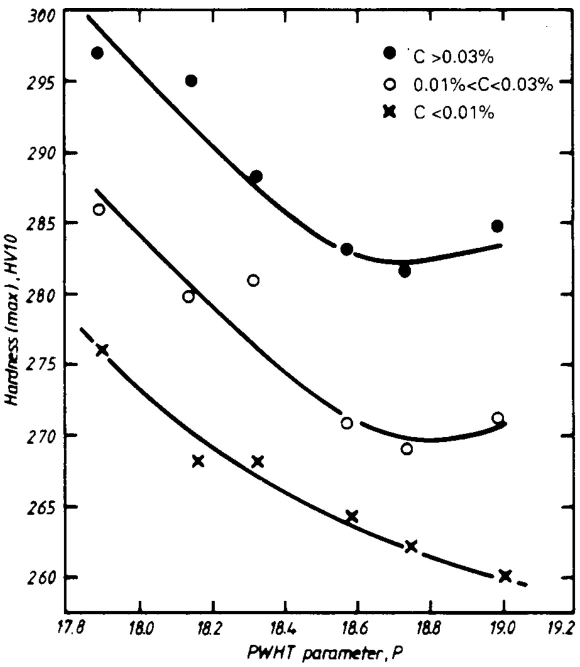


Figure 18: relationship between average weld metal hardness levels (maximum value for each weld) and PWHT parameter, $P = T(20 + \log t) X 10^{-3}$: hardness data divided in terms of deposit carbon content [29].

7.6 Corrosion resistance

Alloys of the 13%Cr-4%Ni type were developed in the early 1960's as a cast replacement for the many applications where the CA15 (410) alloy had traditionally been used. The CA15 alloy was more difficult to process in the foundry and exhibited relatively poor weldability.

The first generation of applications were therefore not intended to exploit any additional benefits in corrosion resistance. The 13/4 steels offered good general corrosion resistance in aqueous environments combined with excellent abrasion/cavitation resistance.

For oil and gas applications the steels offer good performance where there are high levels of CO_2 and can therefore be used as a viable alternative to 410 alloys.

7.6.1 Sour service

These alloys find application for oil and gas production fluids containing CO_2 and H_2S but are potentially susceptible to sulphide stress cracking (SSC) in H_2S environments, particularly in general or localised hardened conditions, e.g. welds. The sensitivity to SSC increases with hardness and NACE MR 0175 limits 13%Cr-4%Ni alloys to 23HRC maximum for use in sour service (see 7.5 above).

Further reductions in carbon content combined with higher alloying up to 6%Ni and 2.5%Mo produce improvements in performance in H_2S environments, and hence lead on to the evolution of the so called "supermartensitic stainless steels" which are dealt with in the next section.

8. SUPERMARTENSITICS

The family of very low carbon supermartensitic steels can be further subdivided into three groups of increasing alloy content to provide cost effective materials for a range of operating conditions, particularly increasing sulphide stress cracking (SSC) resistance [51]. In Table 4 the three groups described in the literature are sub-divided into "lean", "medium" and "high" alloy types:-

Table 4A "Lean" supermartensitics with 11%Cr-2%Ni, no Mo

GRADE TRADE NAME	Composition, weight %									Producer/reference
	C	Mn	Si	Cr	Ni	Mo	Cu	N	Others	
Fafer X80 11Cr-2Ni	0.015	1.7	0.2	10.5	1.8	<0.1	0.5	<0.012	-	CLI-Fafer [51, 52]
KL-12Cr-X80	0.01	1.2	0.2	11	1.5	-	0.5	<0.012	-	Kawasaki [53]

Table 4B "Medium" supermartensitics with 12%Cr-4.5%Ni-1.5%Mo

GRADE TRADE NAME	Composition, weight %									Producer/reference
	C	Mn	Si	Cr	Ni	Mo	Cu	N	Others	
Super 13Cr-M	0.01	0.4	0.2	13	5	0.7	-	-	Ti - 0.1	Sumitomo [54]
Fafer X80 12Cr4-5Ni1-5Mo	0.015	1.7	0.2	11.5	4.5	1.4	0.5	<0.012	-	CLI-Fafer [51, 52]
"Sweet" 1%Mo	<0.015	0.5	0.2	11	3.5	1	-	<0.01	Ti - 0.03	Nippon Steel [55]
'F2NM'	0.01	0.6	0.4	13.4	3.8	0.4	-	0.015	-	Vallourec [56]
'HP13Cr'	<0.03	0.4	<0.3	13	4	1	-	0.05	-	Kawasaki [47, 57, 58, 59]
'D 13.5.2N'	0.02	0.7	0.3	13.3	4.8	1.6	0.1	0.08	-	Dalmine [60, 61]
'CRS' (>95ksi)	0.02	0.5	0.3	12.5	4.5	1.5	1.5	0.02	-	Nippon Steel [62, 63, 64]

Table 4C "High" supermartensitics with 12%Cr-6.5%Ni-2.5%Mo

GRADE TRADE NAME	Composition, weight %									Producer/reference
	C	Mn	Si	Cr	Ni	Mo	Cu	N	Others	
UNS S42416 Super 13Cr-S	0.01	0.4	0.2	12	6.5	2.5	-	-	Ti - 0.1	Sumitomo [54]
Fafer X80 12Cr-6Ni2-5Mo	0.01	1.7	0.4	12	6.5	2.5	-	<0.012	-	CLI-Fafer [51]
KL-HP-12Cr	0.01	0.5	0.3	12.3	5.5	2.1	-	-	-	Kawasaki [65]
"Mild Sour" 2%Mo	<0.015	0.5	0.2	11	5.2	2	0.6	<0.01	Ti – 0.02	Nippon Steel [55]
"Sour" 3%Mo	<0.015	0.5	0.2	11	6	2.5	0.7	<0.01	Ti – 0.02	Nippon steel [55]
'Super 13Cr' (13-5-2)	0.02	0.4	0.2	12.5	5	2	-	<0.08	-	Sumitomo [66, 67, 68, 69, 70]
'Super 13Cr' (13-6-2.5-Ti)	<0.01	0.4	0.3	12	6.2	2.5	-	<0.01	Ti - 0.06 or 0.3	Sumitomo [71, 72, 73]
'Super 13Cr' (12-5-2)	0.02	0.5	0.2	12.2	5.5	2	0.2	0.02	V - 0.2	British Steel [56, 74]

Note to Table 4A-C: Steels shown above the heavy lines are all taken from recent (1999) literature, and are probably representative of compositions at the time of writing. Those below the line are from the period 1993-98, and are representative of earlier compositions, some of which may have been development or experimental steels.

8.1 Microstructure

The microstructures of these steels are of low or very low carbon 'soft' tempered martensite (Fig. 19), with inherently high strength and toughness. Some finely dispersed austenite but little, if any, ferrite will be present.

Typical Ac_1 together with Ms and Mf temperatures for the three groups are shown below [51].

Transformation temp. °C	Lean	Medium	High
Ms	360	250	150
Mf	220	120	30
Ac_1	650	640	630

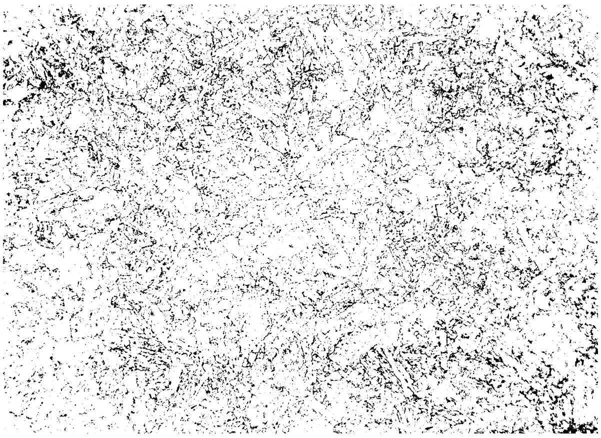


Figure 19 Microstructure of 0.01%C-12.6%Cr-6.4%Ni-2.1%Mo supermartensitic steel. x200

8.2 Mechanical Properties

Many of the grades can be supplied to two or more specified minimum proof stress levels as demanded by the market for oilfield tubular goods. Like the lower nickel soft martensitics, these alloys have a high resistance to softening by heat treatment, and very high strengths are easily obtained.

8.2.1 Strength

Figure 20 is a simplified version of Figure 1, and shows the range of tensile and 0.2% proof strengths which are typical of the supermartensitic steels. The most commonly used grade for flowlines, etc., at the present time (1999) is X80, which is at the bottom end of the strength range for these steels. However, it is known that the users would like to exploit the higher strength grades to save cost and weight, and X100 is certainly a viable proposition provided suitable welding consumables and procedures can be developed (see Section 8.5). Yield/proof strengths in excess of 700 MPa can be readily achieved with the medium and high alloy grades [51].

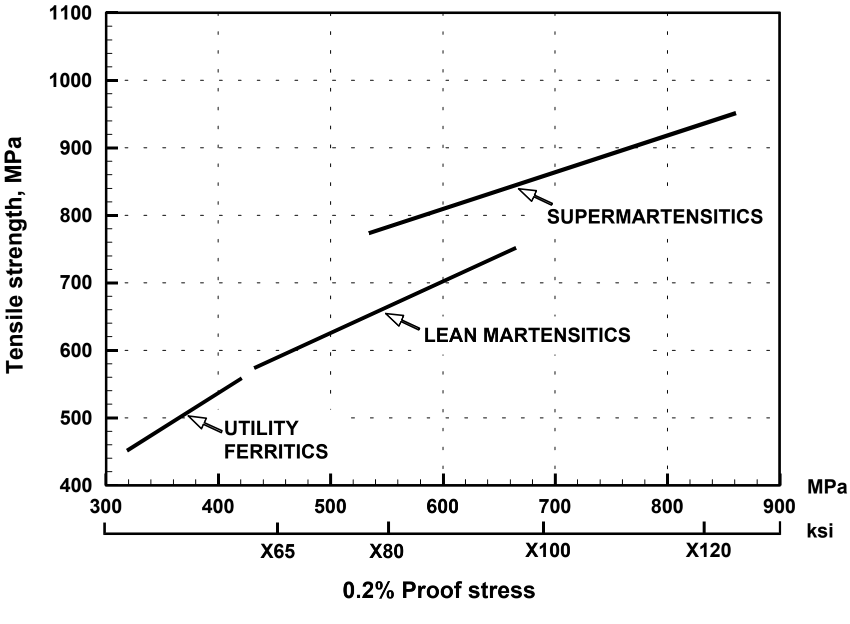


Fig. 20 Tensile strength/proof stress relationship for supermartensitics shown in relation to lean martensitics and utility ferritic steels. Note that the strength of some lean supermartensitics may be close to the lean martensitics.

8.2.2 Toughness

Provided that the correct tempering treatment is carried out (close to the Ac_1), excellent toughness can be achieved in the parent steels. It is generally considered that the lean grades are suitable for design/service temperatures down to –20^{O}C, whereas the medium and high grades are suitable down to –40/-50^{O}C, the temperatures commonly specified for offshore oil and gas projects.

Typical impact (transition) curves are shown in Figure 20. From these it can be seen that there is some evidence that medium grades are slightly tougher than the high alloy grades. However, all grades show impact values in excess of 100J at –80^{O}C, and only the lean grade shows a steeper transitional behaviour at the extreme lower temperatures.

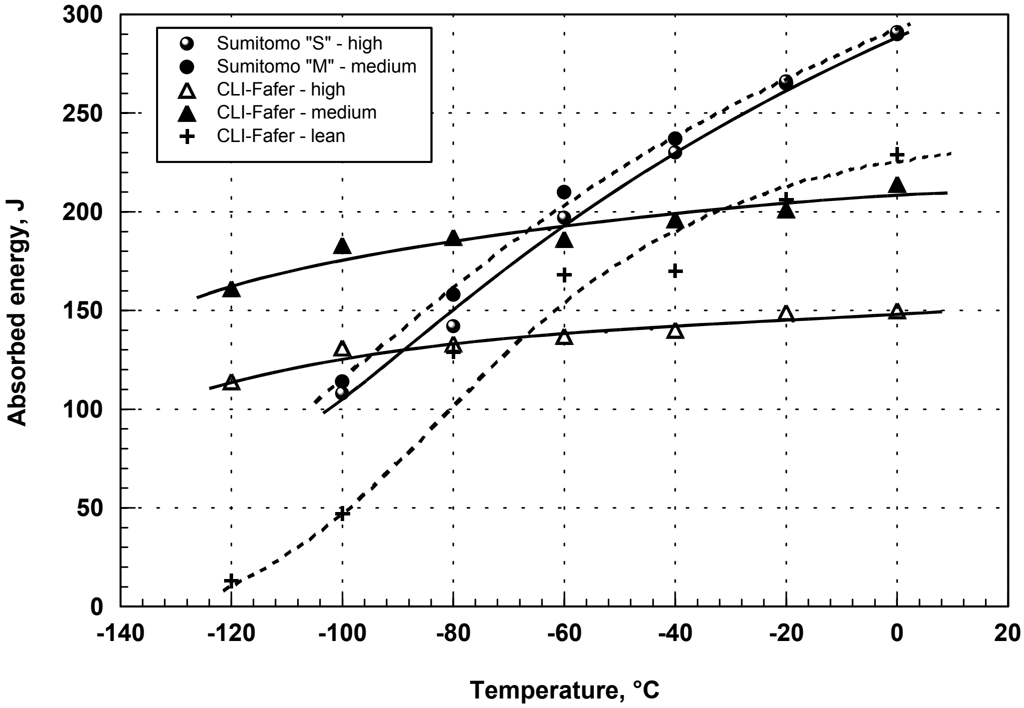


Figure 21. Impact/transition temperature curves plotted from published data from two suppliers for various supermartensitic grades of steel.

8.2.3 Elevated Temperature Properties

A number of flowlines are designed to operate with "hot" product and may have an operational design requirement up to 250^{O}C [75]. The supermartensitic steels exhibit good elevated temperature properties, relative to duplex stainless steels. For example, the high alloy grades show about a 15% reduction in 0.2% proof strength over the temperature range +20^{O}C to +250^{O}C, whereas duplex and superduplex stainless steels show a reduction of 25-30% over the same temperature range.

8.3 Product Forms

Supermartensitics are predominantly supplied as seamless tube used mainly for small diameter flowlines, although there are now a number of producers of plate and bar. Larger diameter welded pipe is now available [76, 77, 78], and a range of fittings and flanges are being developed [79].

8.4 Applications

The main applications are for linepipes, flowlines, tube bundles and downhole tubulars requiring high strength combined with good resistance to corrosion by dissolved CO_2, often under saline conditions, with useful resistance to pitting and SSC in the presence of some H_2S, dependent upon the grade chosen.

For these applications supermartensitics occupy a potentially economic niche between carbon/low alloy steels and the more expensive CRA's [80].

As experience and confidence in these steels develops, it is expected that they may find wider application where their combination of strength and corrosion resistance can be economically exploited, e.g. pipeline pig traps and launchers.

8.5 Welding

A key characteristic of the new supermartensitic steels is their excellent weldability. As can be seen from Table 4-3, they are produced with very low carbon contents, in some cases down to <0.005% and low nitrogen contents of <0.01%. This combination of low interstitials has the potential to give HAZs of low hardening response and high toughness which, in turn, leads to the practical benefit of avoiding the need for pre-heating or post weld heat treatment (PWHT). These steels are sensitive to magnetisation particularly when handled and stored in line with the earth's magnetic field. This residual magnetism can result in severe arc blow and precautions such as degaussing may be necessary.

Choice of weld metal is largely governed by the need to meet the high parent steel proof stress combined with adequate toughness. There are essentially three approaches to the welding of these supermartensitic steels, namely:

a) Duplex/superduplex consumables

The use of duplex and superduplex alloy weld metals which can achieve satisfactory strength (i.e. 550 MPa yield/proof strength, or X80 minimum at room temperature) and overmatch the corrosion requirements. They are available in a wide range of consumable types for all the major arc welding processes, and already have a well-established track record in the offshore oil and gas industry (Fig 22).

Figure 22: Weld fusion line and HAZ of a supermartensitic steel welded with 25%Cr superduplex filler metal x500

b) Matching consumables

The use of matching or nearly matching composition weld metal is an area of active development for which the overwhelming driving force is the potential ability to overmatch the strength of the parent steel, particularly at elevated temperatures up to about 200^{O}C. As previously stated, there is significant interest in the use of these steels at the X100 level, which is a higher strength than can be achieved with 25%Cr superduplex weld metals (see Figure 23).

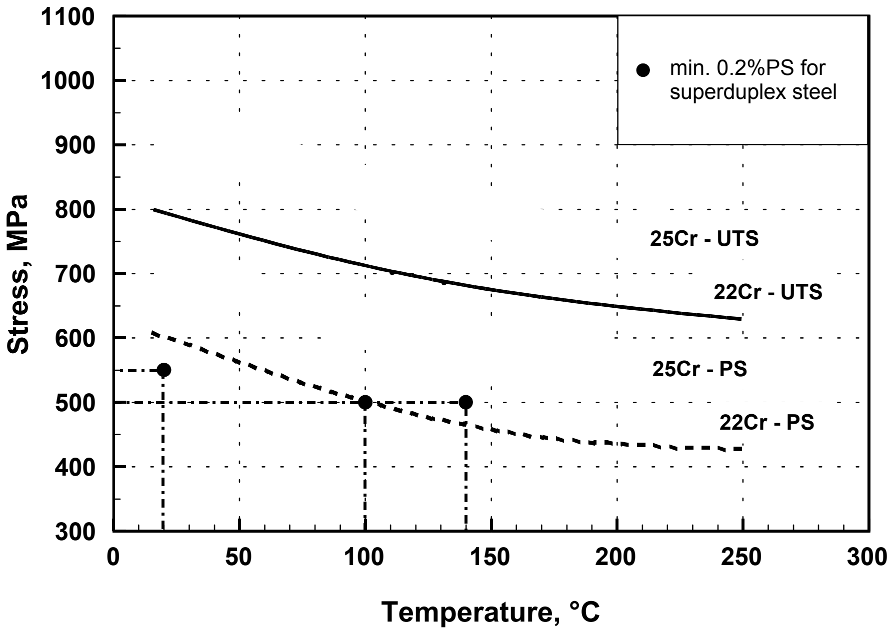


Figure 23. Typical elevated temperature tensile properties for 25%Cr superduplex and 22%Cr duplex stainless steel weld metals together with minimum specified proof stress for superduplex parent steel at elevated temperature.

c) Alternative welding methods

The following processes are being actively developed and show significant potential for supermartensitic pipes/flowlines: electron beam welding for longitudinal welds [77], laser welding for both longitudinal and circumferential welds [52, 78] and radial friction welding [65] for circumferential welds.

8.5.1 Welding consumables, processes and properties

a) Duplex/superduplex consumables

Duplex and superduplex welding consumables are available for all the established arc welding processes, and have been used for both the manufacture of longitudinally welded pipe and circumferential butt welding of pipelines and flow lines used in a number of projects over the last few years [81, 82].

Welding is normally carried out without preheat, and sometimes without PWHT, although in some cases a short 5 min PWHT at 650^{O}C has been applied to soften the HAZ peak hardnesses without having a detrimental effect on the superduplex or duplex weld metal microstructure and toughness. Control of interpass temperature and heat input is generally similar to that for welding duplex alloys, i.e. 100-150^{O}C and 0.5 - 1.5kJ/mm.

Weld metal toughness meets current offshore specifications with GTAW deposits usually giving impact values comparable to the parent material and the higher oxygen content fluxed processes, particularly SMAW and SAW, being substantially lower (Fig. 24).

Hardness values are generally in the range 260-300 HV for 22%Cr duplex and 290-320HV for 25%Cr superduplex weld metals.

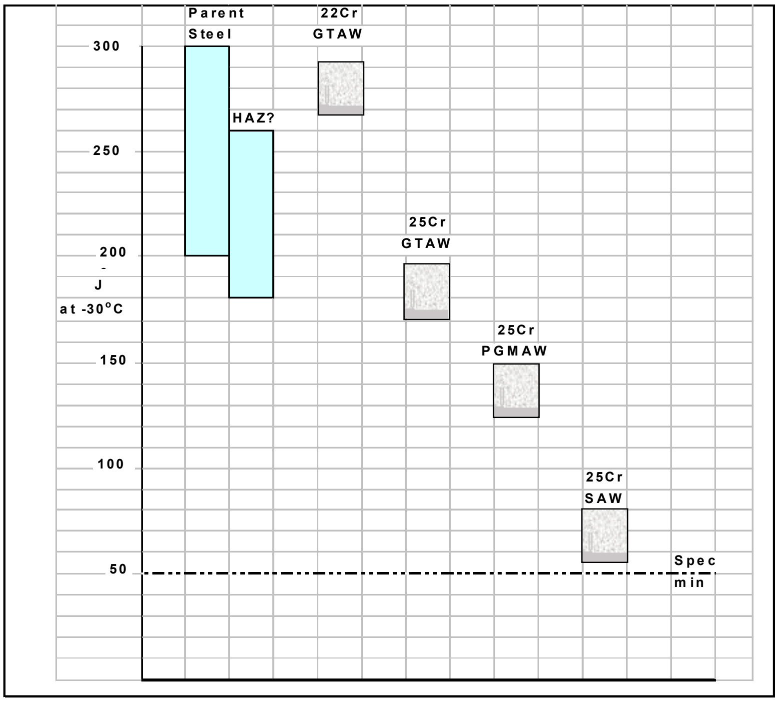


Figure 24: Typical impact values at –30°C for supermartensitic parent material and HAZ shown in comparison with 25%Cr and 22%Cr duplex weld metals from a number of processes.

b) "Matching" composition consumables

Matching composition consumables are an active area of development, and a substantial amount of promising data has now been published [11, 32, 55] However, at the time of writing (1999) the use of matching consumables had been restricted to welding procedure development work. They have not yet been used for the welding of supermartensitic flowlines.

Most of the development work has concentrated on the design of solid or metal cored wires (MCW) for use with the GTAW, SMAW or SAW processes.

Oxygen content of the weld deposit has a significant effect on impact toughness and from Fig 25 it can be seen that in the as-welded condition only the gas shielded processes would achieve a requirement of 40J at -40^{O}C [11].

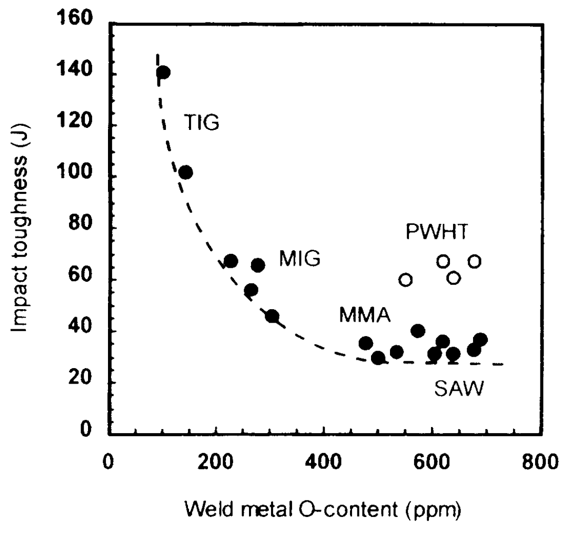


Figure 25: Dependence of Charpy-V impact toughness at -40^{O}C of Mo-alloyed supermartensitic weld metals on oxygen content and PWHT [11].

Similar results were reported with solid wires, with difficulties being encountered in achieving adequate weld metal toughness with submerged arc deposits, particularly in the as-welded condition [32].

The gas shielded processes, particularly TIG, give values up to around 100J at -40^{O}C. However, with MIG welding, the use of oxidising shielding gases (e.g. Ar + 2% O_2) to improve arc behaviour/weld metal transfer, has the effect of increasing weld metal oxygen content and reducing toughness by about 50%.

It is well recognised [11, 81, 83] that the weld metals should have a predominantly martensitic microstructure with a minimum of retained austenite and delta ferrite, both of which have a potentially detrimental effect on mechanical properties. To achieve this, particularly in multipass welds, requires very careful control of composition, since the compositional range for a “fully” martensitic microstructure is very limited. The ferrite factor itself must be restricted to minimise the formation of ferrite but, in addition, a mixed solidification mode should also be avoided to prevent segregation and hence reduced homogeneity. In addition, the more highly alloyed grades have an increased tendency to contain retained austenite. The constitutional diagram relevant to these supermartensitic weld metals has already been described in Section 4.2.4 and illustrated in Figure 15.

Because of the potential complexity of the alloy system, most development work on matching consumables has been concentrated on the “high” alloy types (12%Cr-6%Ni-2.5%Mo) on the assumption that these could also be used for the “lean” or “medium” grades as required. However, the work by Karlsson et al [11] presents work on a variety of compositions with molybdenum contents ranging from 0% up to about 2.5% and they suggest that “matching” compositions should be used for the “medium” and “high” alloy grades where practicable.

Most workers report matching weld metal yield/proof strengths in the range 750 to 850 MPa, which is more than adequate for X100 material. However, the Japanese workers from Nippon Steel [55] report weld metal yield/proof strengths in the range 660 – 670 MPa, which is surprisingly low and, although suitable for X80, is significantly lower than that reported by others. Although the detailed composition of the weld metal is not given, the relatively high nickel content of 7.5% would suggest the presence of retained austenite, and hence a reduced strength as noted by Karlsson et al [11].

In the Japanese work Asahi et al [55] also comment on the presence of delta ferrite to suppress the risk of hot cracking, although there have been no other reports or suggestions that indicate that hot cracking would be a potential problem in these low carbon martensitic weld metals.

Hardness values in the weld metals are consistent with the high strengths, with values being reported in the range 300-380HV. As would be expected from Figure 9b – higher values tend to be associated with higher carbon levels. Heuser et al [32] demonstrate the effect, and clearly show maximum weld metal hardness rising from just over 300HV at 0.007%C to about 340HV at 0.015%C.

8.5.2 HAZ Properties

The major influence on HAZ properties is the carbon content of the base material (Figure 26), although a small addition of titanium of about 0.1% is reported to reduce the secondary hardening in the grain coarsened region of the HAZ

As has been previously indicated, limited time WHT's have been carried out to reduce peak hardnesses in the HAZ, and detailed reports on the HAZ response to PWHT can be found in reference 85. Since the HAZ is taken above the Ac_1 temperature, and then quenched to untempered martensite, there is negligible effect of welding heat input, although there will be some tempering (softening) in multipass welds. As the hardness increases, then so does the strength, with a corresponding reduction in toughness.

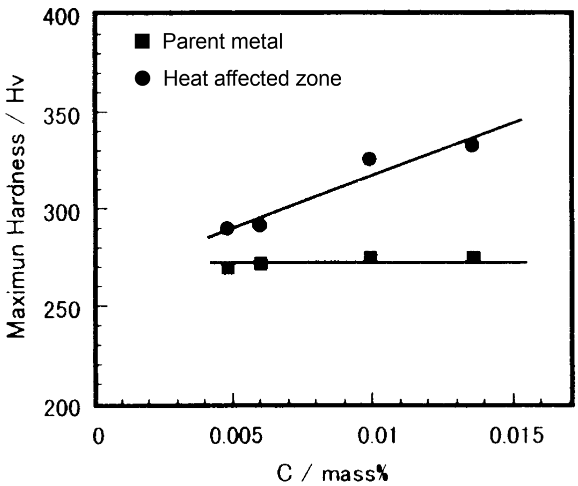


Figure 26: Effect of carbon content on the maximum hardness in parent metal and the heat affected zone [54]

However, all the published work shows that HAZ impact values, although lower than the parent material, are more than adequate to meet specifications down to –40/-50^{O}C. As in the case of the parent steels, the lean grades tend to have lower HAZ toughness than the medium or high grades.

8.5.3 Avoidance of hydrogen cracking

There has been at least one report of hydrogen cracking initiating in the grain coarsened HAZ of supermartensitic stainless steel weldments [85]. The TIG (GTAW) welds, made using superduplex filler material, were used to join prefabricated lengths of flowline prior to reeling of the pipe on the laybarge. It is assumed that the failures resulted from a combination of relatively high HAZ hardness, the presence of some hydrogen, and comparatively high strains caused by the reeling operation. Since, in the absence of PWHT, neither high HAZ hardness in the range 300-350HV nor high strains arising from the reeling operation can be avoided, the only solution to the problem is to reduce the hydrogen content of the filler metal. This can be achieved by either avoiding pick up of hydrogen during the annealing stages of the wire processing operation or by degassing the filler wire at 1050°C on completion of manufacture.

Superduplex filler metals with guaranteed low levels of hydrogen (<5ppm) are now available for these critical applications. It is also prudent to reduce the risk of hydrogen pick up from other sources, e.g. shielding gas moisture content [85, 86].

8.6 Structural Integrity

Since the weldable supermartensitic steels are relatively new, there is limited fracture toughness data available, although it is known that a number of test programmes are underway. The most complete fracture toughness studies, including both CTOD and wide plate testing, are those reported by CLI-Fafer [51]. They indicate that CTOD values in excess of 0.2mm can be expected for both bulk weld metal and fusion lines in both lean and medium grades. Typical specification values would be a minimum of 0.15mm at the test/design temperature [75].

Wide plate tests give in most cases greater than 2% plastic strain at maximum load, with significant crack path deviation from the initiating site, i.e. weld metal or HAZ. Similar results have recently been reported on wide plate tests using laser welds, adding further confidence to the high level of toughness and therefore safety inherent in these modern supermartensitic steels.

8.7 Corrosion Resistance

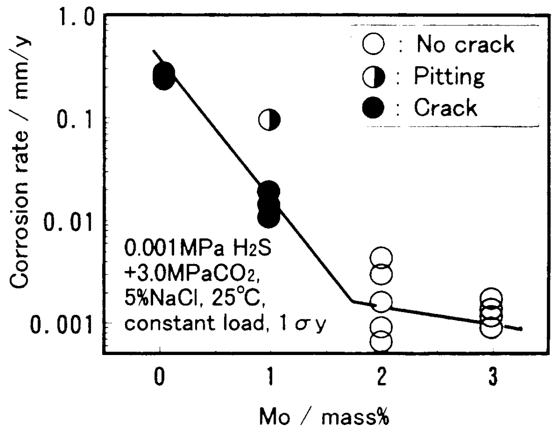
It is not the intention of this document to review the complex issue of the corrosion behaviour of supermartensitic steels. For more detailed and comprehensive studies, the reader is referred to the many papers published by NACE and the proceedings of the conference "Supermartensitic Stainless Steels '99".

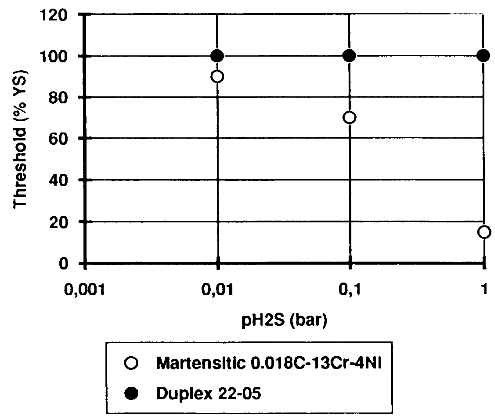
8.7.1 General corrosion

The supermartensitics exhibit significantly lower rates of general corrosion than the standard type 420 steels. This is attributed to the lower carbon content of the 'super' grades, which combines with less chromium as carbides, and the beneficial effects of molybdenum and possibly other alloying elements such as copper. An independent test programme examined a number of steels of the medium and high alloy types [87], using the environmental limits in MR0175 of pH ≥ 3.5, and an H_2S partial pressure of ≤0.1 bar (0.01 MPa) with chloride levels in excess of 10^5ppm. Results indicated that the general corrosion rates for the supermartensitics are typically 10 to 20 times lower than for the standard 420 steels. However, the pitting rates are reduced by a smaller margin and, in the light of these findings, the proposed maximum operating temperature (under the test conditions) is limited to 180°C. This is rather lower than the maximum temperature indicated by some manufacturers and specified for some applications, but with rather less onerous operating or test conditions [75].

8.7.2 Sulphide stress cracking (SSC)

It has been reported [87] that these steels are not immune to hydrogen cracking under cathodic protection. Welded samples have shown cracking initiating from pits in locally rough or damaged areas in HAZs under normal cathodic conditions (~900mV vs Ag/AgCl). It appears that it may be necessary to restrict the protection conditions to around 700mV and/or restrict the hardnesses of the HAZs to avoid the risk of cracking in service.





O Martensitic 0.018%C-13%Cr-4%Ni ● Duplex 22%Cr

Figure 27: Effect of Mo content on corrosion rate and SSC susceptibility [54].

Figure 28: Influence of H_2S partial pressure on SSC threshold according to NACE TM01-77 test, for a 13%Cr-4%Ni martensitic stainless steel [89].

The 'lean' supermartensitics, without molybdenum, are not intended for SSC resistance in H_2S environments. However, most of the manufacturers (Table 4B and 4C) of the medium and high grades claim some resistance to SSC. The improvement in resistance to SSC comes from the increasing molybdenum content, presumably improving pitting resistance as a precursor to stress cracking. The effect is well illustrated in Figure 27, except that it should be noted that the partial pressure of H_2S at 0.001 MPa is very low.

Considerable work [88] has been carried out on unwelded material and has shown that the supermartensitic steels appear to be sensitive to SSC at 90% of yield strength, particularly at room temperature. However, sensitivity may be a complex function of chloride content, pH and temperature, and it may be possible to establish suitable safe limits at lower stress levels. The importance of stress level on SSC threshold in soft martensitic steels is illustrated in Figure 28 [89].

8.7.3 Corrosion resistance of welded joints

In spite of the fact that the new very low carbon supermartensitics are promoted as weldable steels, there is much less corrosion data available for welded joints than for parent steels. Some manufacturers [55, 89, 90] have carried out testing programmes and, of course, some testing laboratories acting on their behalf have recognised the critical nature of the welded joint [91].

The conclusions from the above work, most of which used duplex or superduplex welding consumables, can be summarised as follows:-

- Duplex or superduplex weld metal shows superior corrosion resistance to the parent supermartensitic steel – as would be expected.
- The HAZ is generally identified as the weak link – particularly with high hardness values – hence the use of short time (5-10 min.) PWHT to reduce peak hardness, and the incentive to produce extra low carbon steels to avoid very high HAZ hardnesses in the first place.
- Attempts have been made to avoid the risk of SSC in welded joints, since performance depends critically on combinations of pH, chloride level, temperature and stress level. Some workers have attempted to indicate crack/no crack boundaries for welded joints under various conditions and these are given in Figure 29. More recent work [92] has proposed limiting conditions for a 12%Cr, 6%Ni, 2%Mo steel for a range of H_2S partial pressures and pH (Figure 30).

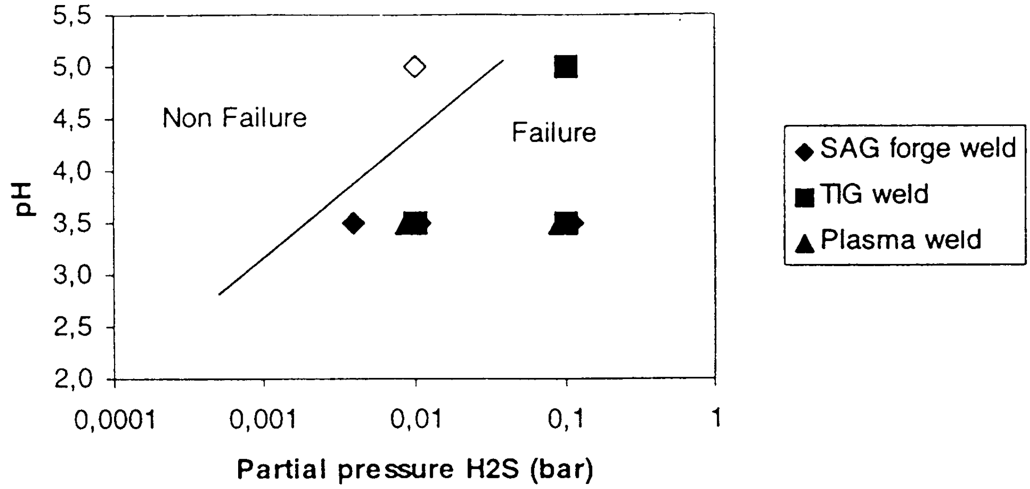


Figure 29a: Environmental limits for welded specimens of super 13%Cr SS tested in buffered NaCl solution at room temperature. Specimens are PWHT at 625^{O}C for 3-10 minutes. Open marks indicate non-failure, while filled marks are registered failures [91]

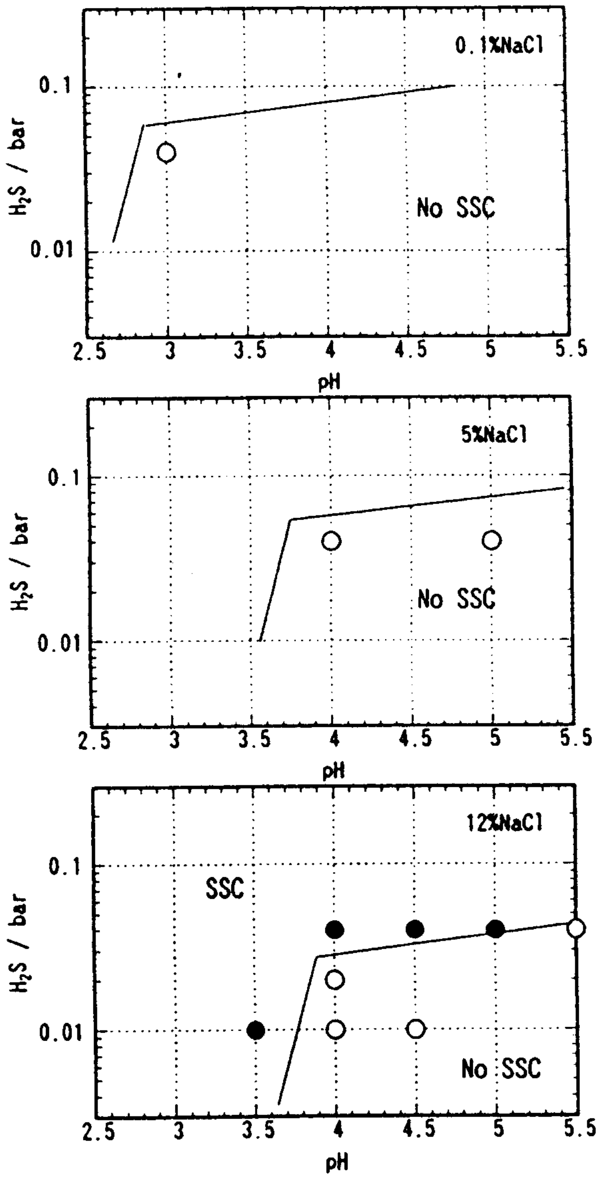


Fig 29b: Effects of Cl-, pH and ppH2S on SSC occurrence. 2.5PL-M-M, 4-point bent beam, 100%YS, 25^{O}C, 14 days, machined specimen [55]

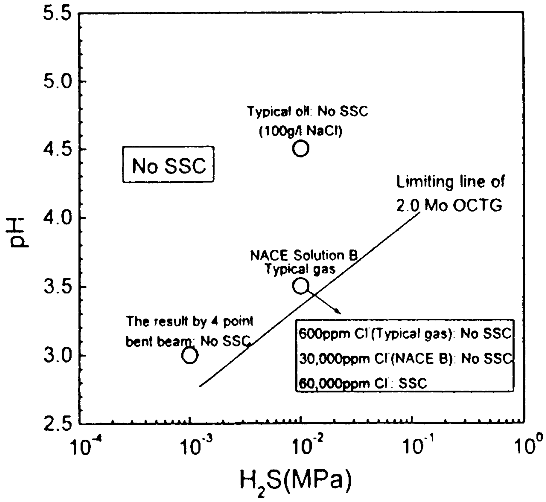


Figure 29c: Effect of H_2S partial pressure and pH on SSC resistance of the welded joint in Steel 13Cr-S (Cyclic SSRT. 25^{O}C, 5%NaCl) [90]

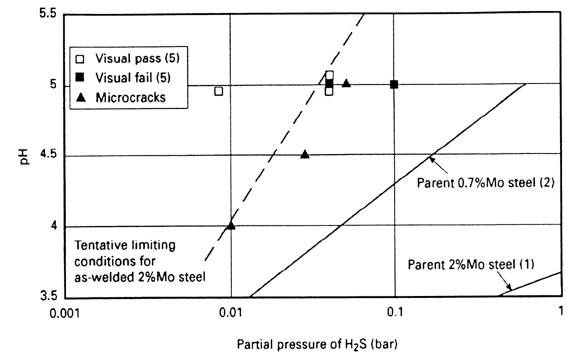


Figure 30: SSC test results and proposed limiting conditions for weldments in 13%Cr-6%Ni-2%Mo-0.1%Ti using superduplex and type 625 filler metal. Indications were at the toe/HAZ region [92]

9. SUMMARY AND CONCLUSIONS

This paper reviews the development of 11-13%Cr ferritic and martensitic stainless steels from the low carbon “utility” ferritics, through the mature “lean” and “soft” martensitic steels up to the recently developed “supermartensitics”. This last group of materials represents a rapidly developing area of technology, and much of the information included in this review is taken from the proceedings of the first international conference on Supermartensitic Stainless Steels held in Brussels in May 1999.

Although key aspects of the review are welding and weldability, these are so intimately connected with the basic metallurgy of this group of steels that a significant part of the document is devoted to a metallurgical overview. This deals with solidification behaviour and transformation control, not only in standard “420 type” alloys, but also in the 12%Cr ferritics and the low carbon martensitics. The ability of the steel maker to control carbon contents to very low levels, together with a greater understanding of the role of additional alloying elements, has lead to the evolution of the modern weldable supermartensitics.

In order to put the metallurgical overview into perspective, the 13%Cr steels have been classified in four groups which provides an opportunity to bring together steels of similar composition and fields of application. Each group contains examples of both generic and proprietary steels (and in some cases steels still under development) and is supported by a commentary which provides basic data on mechanical properties, welding and weldability, structural integrity and corrosion resistance.

From the information provided, the following conclusions can be drawn.

1. The utility ferritic steels have been developed over the last 20 years to the point where they now have a well established part of the steel market. They provide a cost-effective bridge between mild steels (including painted, coated and galvanised steels) and the more expensive 300 series austenitic stainless steels. Welding and fabrication techniques are more than adequate for the range of structural applications to which these steels are best suited, and which exploit their general corrosion behaviour, wet abrasion resistance, and in some cases high temperature scaling resistance.

   There will always be toughness limitations in weld HAZs, and for this reason these steels are not used in critical pressure containing structures, although with suitable precautions they are used in other safety critical structures such as road and rail vehicles.

2. The lean martensitics, which include type 420, represent the original 12%Cr martensitic stainless steels and have been widely exploited in a number of industrial sectors because of their combination of corrosion resistance, high strength (at both room and elevated temperatures) and modest cost. They have always had a reputation for being somewhat difficult to weld, and certainly precautions have to be taken to avoid hydrogen cracking, and correct PWHT is essential to achieve adequate HAZ and weld metal properties. The higher carbon type 420 has very little welding history, but has been used extensively for downhole tubulars (unwelded) in the oil and gas industry.

3. The 12%Cr soft martensitics were developed about 40 years ago as cast alloys with about 4% nickel and low carbon, achieved through steelmaking improvements. The resultant tempered lath-type martensite gives an exceptional combination of excellent toughness with high strength and good ductility. This lead to the development of very large complex castings, particularly for heavy section water turbine components, with the added bonus of good weldability. Sensible precautions still have to be taken to ensure freedom from cracking and achievement of adequate weld metal and HAZ properties, but the requirements tend to be less onerous than for the plain carbon lean martensitics. For at least 20 years they have been used in the offshore oil and gas industries, and for these applications careful control of PWHT is essential if the restricted hardness levels required by NACE for sour service are to be achieved.

4. The new supermartensitics offer the potential of high strength, improved corrosion behaviour and excellent weldability, possibly without the need for preheat and PWHT. This is achieved by careful alloy control and microstructural balance in combination with extremely low carbon contents. Three grades are being promoted, a “lean” 11%Cr-2%Ni type, a “medium” 12%Cr-4.5%Ni-1.5%Mo type, and a “high” 12%Cr-6.5%Ni-2.5%Mo type.

5. However, most development work has been concentrated on the "medium" and "high" supermartensitic alloy types, and it is claimed that they offer a cost-effective alternative to duplex/superduplex stainless steels for sub-sea oil and gas flowlines for some applications.
6. Weldability of the supermartensitic steels is very good, particularly in terms of HAZ hardenability and risk of hydrogen cracking. However, practical exploitation to date has relied on the use of non-matching duplex/superduplex welding consumables in combination with limited short time PWHT. There is considerable interest in the design and use of matching composition consumables, primarily to overmatch the strength of the current X80 materials, and also to facilitate the possible future exploitation of higher strength grades, e.g. X100. The work has reached a stage where compositions have been defined, substantial testing has been carried out, satisfactory weldment properties have been obtained, and welding procedures are being developed. However, by mid 1999 there were no reports of matching composition supermartensitic consumables being used for a real practical application.
7. Claims are made by the producers that the "medium" and "high" supermartensitic grades offer some resistance to SSC, but the limiting conditions of H_2S content, in combination with chloride level, pH and temperature for welded joints are currently being established.
8. The supermartensitic steels still represent an area of active development, and may warrant a further updated review in a few years' time.

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