FILLER MATERIALS FOR 6%Mo SUPERAUSTENITIC STAINLESS STEELS

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superaustenitic stainless steels

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Filler materials for 6%Mo superaustenitic stainless steels

1 Introduction

As the chemical industry developed in the 20th Century, so the need for increasingly corrosion resistant alloys grew. The effect of molybdenum on improving pitting and crevice corrosion resistance and the influence of nitrogen on stabilising austenite in stainless steels were combined to form a series of alloys widely known as superaustenitics. The beneficial effect of Mo and N on pitting corrosion resistance is demonstrated in Figure 1. The starting point was a development of type 317L – which in turn was an evolutionary development of type 316L – in the form of a grade known as type 317LMN. This stainless steel has about 4.5% molybdenum and 0.15% nitrogen. It was followed by a development known as 904L in which there was increased chromium and nickel and an introduction of copper for improved corrosion resistance in certain acid environments. The typical composition of these two grades is shown in Table 1. Reference is also made to the pitting resistance equivalent number (PRE_N) and this is based on Cr + 3.3Mo + 16N.

The demands of the pulp and paper industry, particularly in Scandinavia, led to the introduction of the so-called 6% molybdenum superaustenitics which in turn led onto the more recent development of stainless steels with up to 7.5% molybdenum and 0.5% nitrogen as shown in tables 2 and 3.

The latest generation fully austenitic stainless steels with elevated, 6-7%, molybdenum alloying and a higher nitrogen level (and possibly increased Mn), show significantly improved resistance to crevice and pitting corrosion attack, during prolonged exposure to media containing high levels of chloride ions. They are also significantly stronger and have a 0.2% proof strength which is about 40% higher than that of the 6% Mo grades.

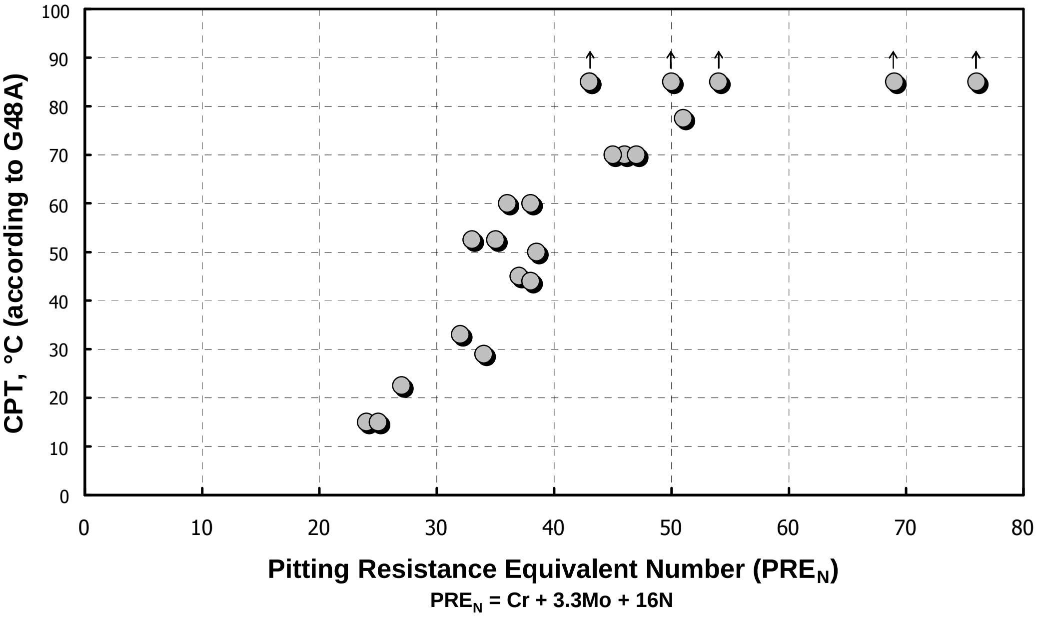


Figure 1 Correlation between critical pitting temperature (CPT) and pitting resistance equivalent number (PRE$_N$) for base materials

Typical analyses of commercially available alloys, used extensively for pipework and vessel systems in the offshore oil & gas, paper pulp bleaching and flue gas cleaning process industries, are given in Tables 1, 2 & 3. Most of these alloys are also available as castings, which are used for a wide range of pump and valve components for similar industrial applications.

Welding of the early superaustenitic alloy, 904L, was often carried out satisfactorily with matching composition welding consumables. However as the alloying content is increased, so does the segregation of molybdenum in the as-cast weld metal microstructure such that the weld metal corrosion resistance falls well below that of the parent steel. This problem is resolved by solution annealing or by the use of nickel base consumables which can accommodate high molybdenum contents with less segregation than iron base consumables. With higher Mo, even if the nickel base consumables do suffer from segregation, they still match the base material. Table 4 shows the difference in Mo content that is produced in an as-welded microstructure as a result of segregation.

This technical profile describes matching consumables for the lower alloyed materials as well as nickel base consumables for the latest most highly alloyed types.

Table 1 Early superaustenitic stainless steels

UNS	*EN*	*Material*	*C*	*Cr*	*Ni*	*Mo*	*Cu*	*N*	*PRE$_N$*
S31726	1.4439	317LMN	<0.03	19	15	4.5	-	0.15	36
N08904	1.4539	904L (Uddeholme) 2RK65 (Sandvik) Cronifer 1925LC (Krupp-VDM) 254SLX (Outokumpu) B6 and B6M (Usinor Industeel)	<0.02	21	26	4.5	1.5	0.1	37

Table 2 6% molybdenum superaustenitic stainless steels

UNS	EN	Material	C	Cr	Ni	Mo	Cu	N	PRE_N
S31254	1.4547	254SMO (Outokumpu)	0.01	20	18	6.1	0.8	0.20	43
N08367	-	AL-6XN (Allegheny Ludlum)	0.015	20.5	24.0	6.3	0.2	0.22	44
N08926	1.4529	25-6MO (Special Metals)	0.01	20	25	6.5	0.9	0.20	45
N08925	-	Cronifer 1925hMo (Krupp-VDM)	0.01	20.5	25	6.5	0.9	0.19	45

Table 3 Later superaustenitic stainless steels with high molybdenum and/or high manganese and high nitrogen contents

UNS	EN	Material	C	Cr	Ni	Mo	Mn	Cu	W	N	PRE_N
S32654	1.4652	654SMO(Outokumpu)	0.01	24.5	22	7.5	3	0.4	-	0.5	57
S34565	1.4565	-	0.02	24	17	4.5	6	-	-	0.5	47
S31266	-	Uranus B66 (Usinor Industeel)	0.01	24	22	6.0	3	1.5	2	>0.4	>50

Table 4 Mo segregation in weld metal

Weld metal	Bulk Mo content, wt %	Dendrite core, wt%	Interdendritic region, wt%
S31254	6.2	4.2	8.1
ERNiCrMo-3	9.0	7.2	11.6

2 Filler materials for 317LMN and 904L stainless steels (table 5)

Filler metals are based on the concept of matching composition with the 904L types being suitable for welding both 317LMN and 904L. These consumables give a fully austenitic, low carbon weld metal with good resistance to corrosion in sulphuric, phosphoric and other inorganic and organic acids. The weld metal PRE_N values are similar to those of the parent alloys, typically >35, but with molybdenum levels of between 4.5 and 5% there is some risk of segregation. It is therefore recommended that overmatching nickel base consumables are used when optimum performance is required in severe chloride pitting media. (see section 3 below)

Table 5 Welding consumables for 317LMN and 904L

Process	Consumable	AWS	C	Mn	Cr	Ni	Mo	Cu	N	PRE_N
MMA	Ultramet 904L	E385-16	0.025	2	21	25	5	1.8	0.1	39
	Ultramet B904L	E385-15	0.025	2	21	25	4.8	1.8	0.1	38
TIG/MIG	20.25.4.Cu	ER385	0.01	1.7	20	25	4.5	1.5	0.1	36

3 Filler materials for 6%Mo superaustenitic stainless steels

Filler material selection is based, primarily, on ensuring 'over-matching' molybdenum content in the weld deposit. There are also some specifications that impose other weld metal restrictions; for example the NORSOK M601 specification (Revision 3, January 2004) requires Mo>8%, Cr>15%, Cr+Mo>28%, C<0.03% and S<0.020% for weld metals to be used on 6%Mo alloys (eg. S31254).

To compensate for the tendency towards Mo segregation during weld solidification, even in nickel-base alloys, an over-matching Mo content in the filler material is essential. Without this, areas of the weld microstructure could develop significant loss of Mo-alloying (and PRE_N) and be subject to preferential pitting attack in service, Table 4.

High Mo nickel base alloy filler metals are suitable for a number of reasons:

- 9-15%Mo, over-matching consumables, are capable of compensating for any segregation effects, and for maintaining a suitable overall minimum alloying level. In addition nickel base weld metals exhibit a much lower tendency to segregation than iron-base alloys.
- Consumables are readily availability as covered electrodes and as solid wires thus allowing the use of most arc welding processes.

Metrode's product programme includes 3 types of filler metal composition and these are covered in the following sections, and the accompanying data sheets, Appendix 1.

3.1 Alloy 625 consumables (table 6)

Alloy 625 type welding consumables have been successfully used for welding 6%Mo stainless steels for at least 20 years. The 21%Cr-9%Mo nickel base weld deposit satisfies requirements for pitting corrosion performance in 6%Mo joints (G48A >40°C CPT) and provides excellent crevice and stress-corrosion resistance. However, the high niobium level of 3.5% in alloy 625 was originally intended to contribute to the alloy's high temperature creep performance although it also has a positive effect on corrosion resistance, particularly in severe pitting and crevice environments.

In some welding applications, the presence of Nb causes problems that may place restrictions on the weld procedure. It may also adversely affect weld HAZ corrosion performance, albeit under extreme service conditions:

- Nitrogen can diffuse rapidly from the 6%Mo HAZ to the weld metal and result in the formation of niobium nitrides at the weld deposit fusion boundary, leading to some loss of ductility and corrosion resistance.
- The above effect can be enhanced during the post weld solution anneal plus water quench treatment routinely applied to welds in 6%Mo castings (and some thick walled wrought alloy fabrications), and requires the use of lower or nil Nb weld metals to avoid failures in side-bend and cross-weld tensile tests.
- Microfissuring in alloy 625 weld deposits have been linked to the presence of niobium, particularly with thicker section, higher restraint, fabrications welded using high deposition rate, deeper penetration welding processes (eg SAW). Niobium, in conjunction with C and Si, increases the tendency to produce a weld metal solidification temperature range.

Table 6 Alloy 625 welding consumables for 6% Mo superaustenitics

Process	*Consumable*	*AWS*	*BS EN*	*C*	*Mn*	*Cr*	*Ni*	*Mo*	*Nb*	*Fe*	*PRE_N*
MMA	Nimrod 625KS	ENiCrMo-3	ENi6625	0.03	0.8	21.5	64	9	3.5	<1.5	51
TIG/MIG	62-50	ERNiCrMo-3	SNi6625	0.015	0.02	22	65	9	3.5	0.8	52

3.2 Alloy C22 and alloy 59 consumables (table 7)

To ensure optimum corrosion performance in 6%Mo alloys or for joints in 7%Mo or high nitrogen alloys such as those shown in table 3, the use of alloy C22 consumables is preferred. Alloy C22 with ~15%Mo ensures that even allowing for micro-segregation the alloy content of the weld metal will more than match that of these higher alloyed superaustenitic stainless steels, with a CPT comfortably over 50°C even in the as-welded condition.

Alloy 59 consumables are also suitable for welding 6-7%Mo base materials and meet the same requirements as C22, but are generally not as readily available.

Table 7 Alloy C22 and alloy 59 welding consumables for 6% Mo superaustenitic and for higher alloyed superaustenitic alloys

Process	*Consumable*	*AWS*	*BS EN*	*C*	*Mn*	*Cr*	*Ni*	*Mo*	*W*	*Fe*	*PRE$_N$*
MMA	Nimrod C22KS	ENiCrMo-10	ENi6022	0.01	0.5	21	49	14	3	4	65
TIG	HAS C22	ERNiCrMo-10	SNi6022	0.003	0.2	21	56	13.5	3	4	65
MMA	Nimrod 59KS	ENiCrMo-13	ENi6059	0.01	0.5	23	60	15.5	-	1	75
TIG/MIG	HAS 59	ERNiCrMo-13	SNi6059	0.003	0.2	23	60	15.5	-	0.4	75

3.3 Metrode electrode 20.18.6.Cu.R (table 8)

Metrode 20.18.6.Cu.R electrode, based on a 6%Mo stainless steel composition matching S31254, is recommended as an economic alternative to nickel base alloys in certain circumstances. It is only suitable for welding castings and thick section wrought components where post-weld solution annealing heat treatment is a mandatory requirement. The heat treatment is essential to ensure homogenisation of the weld metal, and without which severe segregation of molybdenum would remain in the as-deposited weld metal.

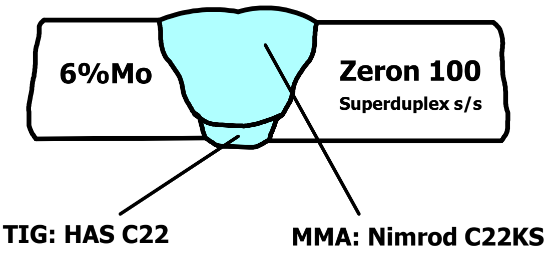
Table 8 All weld metal composition of Metrode 20.18.6.Cu.R

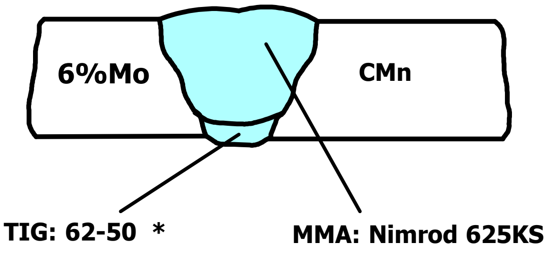
Process	*Consumable*	*C*	*Mn*	*Cr*	*Ni*	*Mo*	*Cu*	*N*	*PRE$_N$*
MMA	20.18.6.Cu.R	0.025	0.7	20	18	6.5	0.7	0.2	45

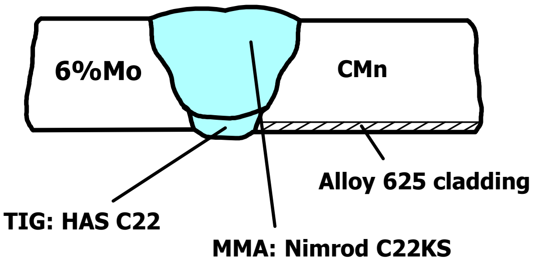
4 Filler materials for latest alloys

The latest materials developed (7%Mo or higher nitrogen - Table 3) require the use of consumables with higher Mo (~15%). This dictates that alloy C22 or alloy 59 consumables should be used rather than 625 consumables in order to achieve weld metal corrosion properties that match those of the base material.

5 Dissimilar welds involving superaustenitic stainless steels







* The alloy C22 or alloy 59 consumables would also be suitable.

Alloy 625 filler materials are recommended for joints involving dissimilar combinations of 6%Mo stainless steel and CMn steel, where the principal requirement is a sound metallurgical bond.

Alloy C22 filler materials are recommended for joints involving dissimilar combinations of 6%Mo, duplex, superduplex stainless steel and nickel-base alloys, together with specific corrosion resistance requirements.

6 Welding process recommendations

6.1 TIG (GTAW)

This process is usually preferred for welding 6%Mo superaustenitic stainless steel pipework, thin materials and small vessels and particular features are:

- suitable for all positions
- enables the precise control essential to achieve single-side root weld deposits both with satisfactory underbead profile, and appropriate pitting resistant weld/HAZ microstructure. 1.6mm diameter filler wire is recommended for wall thicknesses up to 3mm, and 2.4mm diameter for thicker sections
- can be used for higher productivity joint filling, with butt joints in the ASME 5G and 6G positions (BS EN 287 PF and H-L045) using 3.2mm diameter wire, to take advantage of longer run-out and reduced stop/starts, at currents up to 200A, depending on material thickness.
- Argon gas for both shielding and back-purging is recommended.
- Metrode 62-50 & HAS C22 are generally available in 1.6, 2.4 and 3.2 diameter; and HAS 59 is available in 2.4mm diameter.

6.2 MMA (SMAW)

For joint filling in material above ~15mm, the MMA process can be used (Nimrod 625KS, Nimrod C22KS and Nimrod 59KS):

- basic flux coating minimises weld metal oxygen content and so maximise as-welded fracture toughness
- Metrode's 'KS' range of nickel base electrodes optimises operability, particularly in the challenging 5-7 o'clock overhead position of fixed pipe butt joints. Operation on DC+ is required (AC is unsuitable)
- 2.5 and 3.2m diameter electrodes can be used in all positions including ASME 5G/6G positions
- the 4 and 5mm are suitable for downhand welding (note only the Nimrod 625KS is available in 5mm diameter).

20.18.6.Cu.R electrode has a rutile flux coating and is designed for:

- optimum down hand operability for the welding of castings in the flat position in a foundry
- available in 3.2 and 4mm diameter
- post-weld solution annealing, which must be applied when this electrode is used. The heat treatment eliminates segregation and significantly improves weld/HAZ corrosion performance and fracture toughness.

6.3 MIG (GMAW)

The MIG process is not widely used, but where this process can be viably applied for joint-filling, maximum operability and weld deposit are more readily achieved via a combination of:

- pulsed arc, controlled droplet metal transfer (PGMAW), using 1.0mm diameter wire (positionally) or 1.2mm diameter wire (downhand)
- shielding gas mixtures based on high purity Ar + 38%He (<2%CO_2) are necessary to ensure smooth, spatter-free metal transfer.

Where pulsed MIG welding facilities are unavailable, satisfactory operability, albeit only in the downhand position, can be achieved using:

- 1.2mm diameter wire and, typically, 230-240A, 29-30V spray transfer arc conditions
- high purity Argon + 2.5%CO_2.

Metrode 62-50, HAS C22 and HAS 59 is generally available as spooled MIG wire.

6.4 Submerged Arc (SAW)

Submerged arc welding is not widely used for welding superaustenitic alloys because of the need to tightly control heat input and interpass temperature. If SAW is to be used for maximum productivity joint filling on 6%Mo vessels and thicker wall pipework fabrication it is therefore subject to procedural constraints. These restraints are imposed to ensure optimum corrosion properties are achieved but also to avoid the risk of solidification and liquation cracking to which fully austenitic weld metal microstructures are inherently sensitive.

An effective approach to welding is based on:

- small diameter (eg 1.6mm) wire in conjunction with low heat inputs and interpass temperature control
- fully basic flux (eg NiCr) to minimise residual weld metal Si, S, P and O_2 levels
- travel speeds that avoid tear-drop shaped weld pools and/or sharp chevron-patterned weld bead ripples, associated with centreline segregation and possible cracking
- weld deposit profiles with a depth/width ratio of $\approx$ 2:1 to minimise weld centreline cracking.

7 Procedural guidelines

Having selected the appropriate consumable and welding process, it is necessary to then use a satisfactory welding procedure. One of the problems encountered when welding 6%Mo superaustenitic alloys is the formation of an 'unmixed zone', Figure 2. This effect cannot be completely overcome but it can be minimised by the use of the correct welding procedure. The 'unmixed zone' is a region along the fusion boundary where the weld metal and molten base material have not completely mixed.

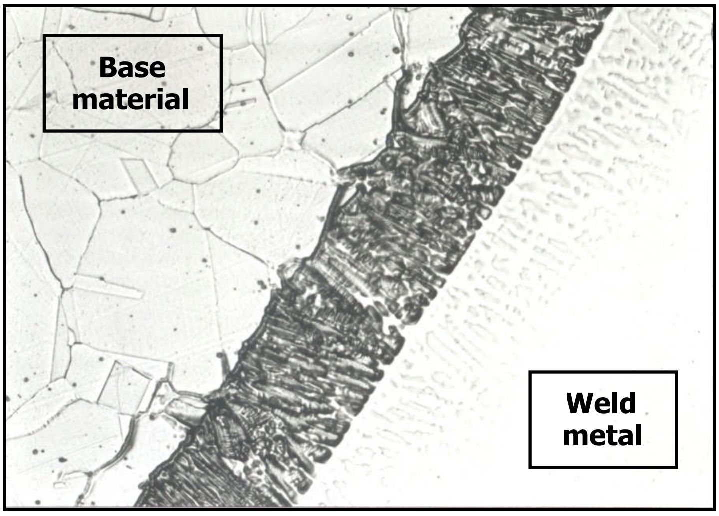


Figure 2 Micrograph showing the unmixed along the fusion boundary

Some regions of this 'unmixed zone' can be lower in alloying than the adjacent base material or weld metal because of segregation. If the 'unmixed zone' is of sufficient width and extends to the surface of the weld, then it can adversely affect the corrosion properties of the joint. To minimise this risk, the width of the 'unmixed zone' must be kept as narrow as possible by the application of the correct welding procedure.

The weld procedure should aim to produce a pitting resistant weld root HAZ microstructure free from Mo segregation and/or intermetallic precipitation. The weld procedure is optimised through control of:

Joint configuration

Typical V-butt in 6" diameter Sch40 (7.11mm WT) pipe would have:

- 70-80°V, 2.5-3mm root gap, 0.5-1.0mm root face.
- establishing consistent fit-up to ensure 360° of reliable weld quality.

Root run

It is recommended that TIG root and 2nd 'cold pass' layers are deposited in a series of equal run-out length weld beads, to avoid the risk of random sections of overheated microstructure within the 360° circumference of the root bead.

- avoiding excessive root melting (and dilution effects) to achieve a full penetration bead
- maximising the amount of filler metal in the root weld deposit
- pure argon should be used as both the shielding gas and the purge gas.

Heat input

This should be limited to 1.0kJ/mm maximum, which minimises fusion boundary and high temperature HAZ alloy segregation, intermetallic precipitation, and also minimises the width of the 'unmixed zone'.

Interpass temperature

This should be controlled to 100°C maximum, which directly influences cooling rate of deposited beads at all stages of welding; this is important to ensure there is minimal risk of intermetallic formation and to reduce the risk of hot cracking in the HAZ of cast alloys.

Weld run-out length

This should be limited to avoid the situation where weld zone background temperature rises to a level above the maximum interpass temperature.

Buttering

In extreme cases where cast alloys are susceptible to cracking in the HAZ it may be necessary to butter the joint faces before filling the joint. The buttering should be deposited with tightly controlled heat input (<1.0kJ/mm) and interpass temperature (<100°C).

8 Mechanical properties

8.1 Tensile strength

The minimum tensile requirements for some selected superaustenitic alloys are given in Table 9 along with the typical values achieved by a range of matching and nickel base weld metals.

Table 9 Typical all-weld metal tensile properties and minimum base material requirements

grade	*Specification UNS or AWS*	*Specification EN*	*Condition **	*UTS MPa*	*0.2% proof stress, MPa*	*Elongation %*
904L	N08904	1.4539	-	530	220	35
Cast 6%Mo	A351 CK3MCuN	-	-	550	260	35
6%Mo	S31254	1.4547	-	650	300	40
25.20.6	NO8926	1.4529	-	650	300	40
7%Mo	S32654	1.4652	-	750	430	35
S3456S	S3456S	1.4565	-	800	420	30
20.25.4.Cu TIG	AWS ER385	W 20 25 5 Cu L	AW	650	490	35
Ultramet 904L	AWS E385-16	E 20 25 5 Cu N L R	AW	620	420	38
Ultramet B904L	AWS E385-15	E 20 25 5 Cu N L B	AW	620	440	38
20.18.6.Cu.R	-	-	SA	715	380	50
62-50 TIG	AWS ERNiCrMo-3	SNi6625	AW	780	520	42
Nimrod 625KS	AWS ENiCrMo-3	ENi6625	AW	800	500	40
HAS C22 TIG	AWS ERNiCrMo-10	SNi6022	AW	770	525	44
Nimrod C22KS	AWS ENiCrMo-10	ENi6022	AW	780	550	36
HAS 59 TIG	AWS ERNiCrMo-13	SNi6059	AW	730	510	34
Nimrod 59KS	AWS ENiCrMo-13	ENi6059	AW	750	520	32

* SA - Solution annealed
AW - As-welded

The only area where some caution may be required in relation to tensile properties is with some of the latest generation high nitrogen wrought alloys (eg S34564). The potential strength of these alloys in wrought form is close that of any of the nickel base alloys; as castings that have been solution annealed the nickel base weld metals should be strong enough.

8.2 Charpy toughness

The fully austenitic nickel base microstructures, deposited using recommended welding consumables are capable of good toughness down to sub-zero temperatures (-196°C). However, results can be subject to the embrittling influences of grain boundary Nb-nitride precipitation at the alloy 625 weld/HAZ fusion boundary, where adequate weld procedure control has not been exercised. The elimination of Nb from alloy C22 filler materials removes this risk and this is reflected in the higher absorbed energy levels reported.

The high alloy fully austenitic stainless steel microstructure of 20.18.6.Cu.R MMA weld deposit, whilst not capable of matching type C22 Ni-base alloy performance, nevertheless shows excellent toughness suitable for the specific application of solution annealed welds in castings. Typical impact properties are given in Table 10.

Table 10 Typical all-weld metal impact properties (as-welded except 20.28.6.Cu.R)

Grade	*specification*	*Test temperature, °C*	*Toughness, J*
20.25.4.Cu TIG	ER385	+20	210
Ultramet 904L	E385-16	-196	50
Ultramet B904L	E385-15	-196	50
20.18.6.Cu.R	-	-50	120
62-50 TIG	ERNiCrMo-3	-196	80
Nimrod 625KS	ENiCrMo-3	-196	60
HAS C22 TIG	ERNiCrMo-10	-196	130
Nimrod C22KS	ENiCrMo-10	-196	45
HAS 59 TIG	ERNiCrMo-13	+20	140
Nimrod 59KS	ENiCrMo-13	-50	50

9 Corrosion performance

9.1 Pitting corrosion resistance

In many fabrications and particularly pipe work the weld root, exposed to the corrosive medium, is the critical region. Both the weld metal and the fusion zone may be adversely affected by welding and it is important to measure the pitting resistance of the weld root and compare it with the base material performance. This is usually done using the ASTM-G48 method A test (6%$FeCl_3$ solution). The typical critical pitting temperature of some materials is given in Table 11, and actual all-weld metal results are in Table 12.

The offshore oil and gas industry typically specify a critical pitting temperature (CPT) of 40 or 50°C using the G48A test.

The latest generation of superaustenitic alloys will not generally show pitting at the maximum G48A test temperature (~85°C) and other test methods would need to be used to evaluate those materials properly.

Table 11 Typical CPT values based on ASTM G48A tests

Material	*Condition*	*CPT, °C **
6%Mo parent material	Solution annealed	65 – 70
Alloy 625 weld metal	As-welded	45 – 50
Alloy C22 & 59 weld metal	As-welded	> 70
20.18.6.Cu.R weld metal	Solution annealed	> 50
S32654	Solution annealed	>85

***** CPT = Critical pitting temperature: temperature at which, after 24 hours exposure, initiation of pitting can be detected or weight loss exceeds 4g/m^2 (or measured on a standard 50mm x 25mm x wall thickness specimen exceeds approximately 20mg)

Table 12 All-weld metal G48A test results

Material	*Condition*	*Test Temperature, °C*	*Weight loss,mg or g/m^2*
20.18.6.Cu.R	Solution annealed	40	1mg (0.3g/m^2)
62-50 TIG	As-welded	40	0
		42.5	0.8 g/m^2
Nimrod 625KS MMA	As-welded	50	0
		52.5	0.9 & 4.2 g/m^2
HAS C22 TIG	As-welded	40	0 & 1mg (0.3g/m^2)
		75	0
Nimrod C22KS MMA	As-welded	40	1mg (0.3g/m^2)