"Superior Properties for Super Duplex Steel Castings, Forgings and Weld Metal"

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Abstract:
Substantial improvements have been made in the impact properties of a super duplex stainless steel (SDSS) through research at Goodwin. This new SDSS, designated 6A-G, has been developed through process techniques and metallurgical controls which enable substantially increased impact properties at standard low temperature and even lower temperatures in castings, forgings and weld metal.

Introduction:
The combination of corrosion, tensile and low temperature impact properties make SDSS a commonly specified material for the oil and gas industry. However metallic phase transformations occur in SDSS in the temperature range of 300°C to 1000°C and this can deleteriously affect impact properties. Such temperature ranges routinely occur in manufacturing processes including during forging operations, castings slow cooling after pouring, welding operations, during quality and post weld heat treatments, and others.

This paper describes the marked improvements achieved in impact properties in both parent and weld metal through closely defined process parameters during the production of SDSS components.

Key significant improvements delivered by 6A-G

> "Greatly increased impact properties at low temperatures in parent and weld metal."

6A-G can be confidently operated to -76°C for section sizes up to 250mm, and as low as -101°C for 100mm section sizes. Table 1: Compares the conventional impact specification for ASTM A890/A995 Grade 6A manufactured in accordance with Norsok M630 MDS D54 and D56, with those that can be specified for the new 6A-G grade.

Table 1: Impact property specification minimum requirement comparison

Material	Test Temperature	Impact Requirements	
		Average min	Single min
ASTM Grade 6A & Norsok M630 MDS D54 & D56	-46°C	45J	35J
6A-G	-46°C	140J*	105J*
6A-G	-76°C	90J*	65J*
6A-G	-101°C	60J*	45J*
*Test location is 1/2T position from a 100mm section			

> "Improved Resistance to Pitting Corrosion."

Table 2: 6A-G performance improvements during G48 method 'A' pitting corrosion test

Material	Coventional test Tempertaure Norosk M630 MDS D54 & D56*	New Test Temperature For 6A-G*
Parent (Forging/Casting)	50°C	60°C
Weld 'as welded'	40°C	50°C
Weld 'PWHT'	50°C	60°C

*Acceptance: weight loss <4g/m^2 with no pitting

Table 2 compares what has historically been specified for SDSS forgings, castings and repairs qualifications for pitting corrosion test temperatures, with what can now be specified for the 6A-G material.

> "Successful Production of Heavier Sections with Improved Impact Strength and Pitting Corrosion Resistance."

The improvements in the 6A-G properties have widened the manufacturing envelope with regards to the section size that can be successfully produced. Testing from the centre section of thick-sectioned test material has confirmed that components up to 300mm can be produced with impact properties meeting the requirements of 45J min average and 35J min single value. The guarantee of meeting these requirements has previously been limited to 200mm or even less.

Compositions:

Typical super duplex wrought and cast grades have a generic composition as detailed in Table 3. As with other SDSS grades they are defined by their chromium and nitrogen additions but differ due to the copper and tungsten content, which improve corrosion resistance in certain applications.

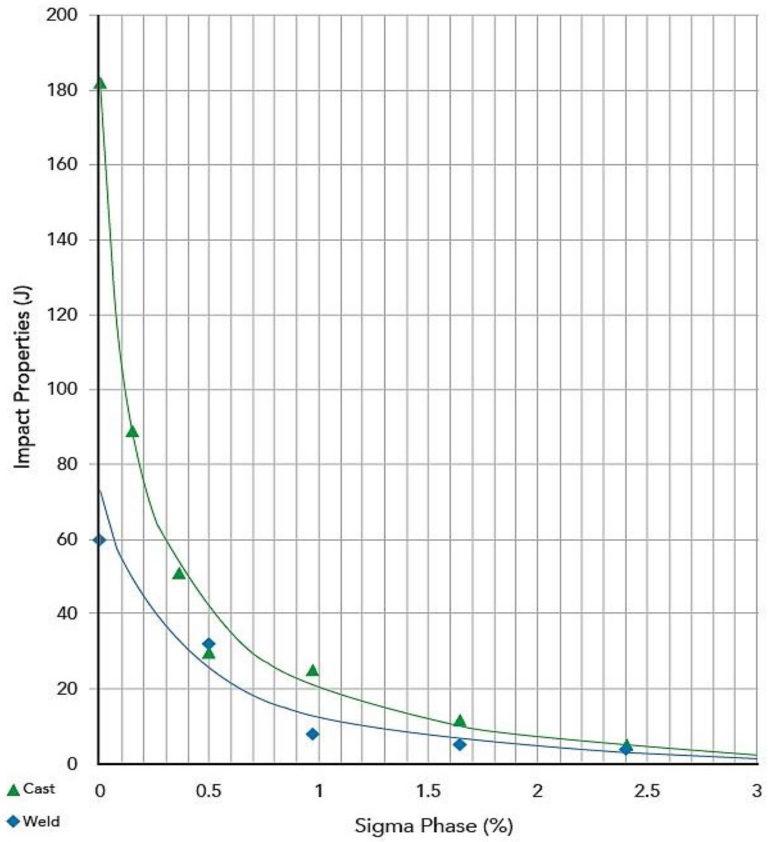
Table 3: Typical SDSS Chemical Specifications (Cu + W Grades)

Material		C	Si	Mn	S	P	Ni	Cr	Cu	W	Mo	N
A995 Gr 6A	Min	-	-	-	-	-	7.0	24.0	0.5	0.5	3.0	0.2
	Max	0.03	1.0	1.0	0.025	0.045	8.5	26.0	1.0	1.0	4.0	0.3
UNS32760	Min	-	-	-	-	-	6.0	24.0	0.5	0.5	3.0	0.2
	Max	0.03	1.0	1.0	0.020	0.03	8.0	26.0	1.0	1.0	4.0	0.3
Zeron100™	Min	-	-	-	-	-	6.0	24.0	0.5	0.5	3.0	0.2
	Max	0.03	1.0	1.0	0.010	0.030	8.0	26.0	1.0	1.0	4.0	0.3
A182 F55	Min	-	-	-	-	-	6.0	24.0	0.5	0.5	3.0	0.2
	Max	0.03	1.0	1.0	0.015	0.035	8.0	26.0	1.0	1.0	4.0	0.3

How does 6A-G work?

The production parameters used to produce Alloy 6A-G limit the development of sigma (σ) and other deleterious precipitates. Sigma phase has a negative effect on the impact properties of SDSS even when present in very small concentrations **[1], [3]**. When 6A-G is compared to the standard 25% chromium SDSS, the standard 25% chromium SDSS contain much higher levels of these deleterious phases in heavy sections. Sigma phase is routinely found at detrimental levels, as high as 1% and above, in the centre of thicker section standard SDSS grades. However, the level in 6A-G in sections of ≤ 200mm are typically < 0.02% and in 6A-G sections of 250mm to 300mm levels of <0.5% are achieved at a comparable rate of cooling.

Figure 1: Graph of impact properties versus sigma phase % in both cast SDSS parent and weld metal when tested at -46°C.



It has been claimed by Topolska & Labanowski that for wrought SDSS up to 8% sigma phase content was allowable, corresponding to a critical impact energy value of 27J for industrial applications **[2]**, however Figure 1 shows the deleterious effect on impact properties of Sigma (σ) phase content at levels well below 8% in cast ASTM A890/A995 6A and standard over-alloyed weld metal in the PWHT state. Similar conclusions to Topolska & Labanowski were made for the maximum allowable sigma phase content for sub-sea pipefittings in SDSS **[2]**. Low temperature impact properties for SDSS of 45J or 60J have generally been specified since around 2009. Goodwins research shows how sigma phase values well below 5% to 8% can cause impact result failures below the industry standard of 35J single and 45J average when tested at -46°C. Sigma values as little as 1.5% to 2% have been shown to result in single figure impact failures.

Figure 1A shows the precipitation of sigma phase in a 300mm section of duplex steel at 1/2T location at different volume % sigma phase.

Figure 1A: **6A-G- 300mm Section 1/2T Location**	**Figure 1B:** **Conventional SDSS – 300mm Section 1/2T location**
≈0.31 % Sigma Phase	≈2.3 % Sigma Phase
	
Sigma precipitaion on the austenite/ ferrite interface	Initiation of sigma precipitaion has commenced as in Fig 1A but then continued to grow into the ferrite phase

Figure 2: 6A-G cast SDSS impact properties over a range of section size in comparison to standard 6A SDSS.

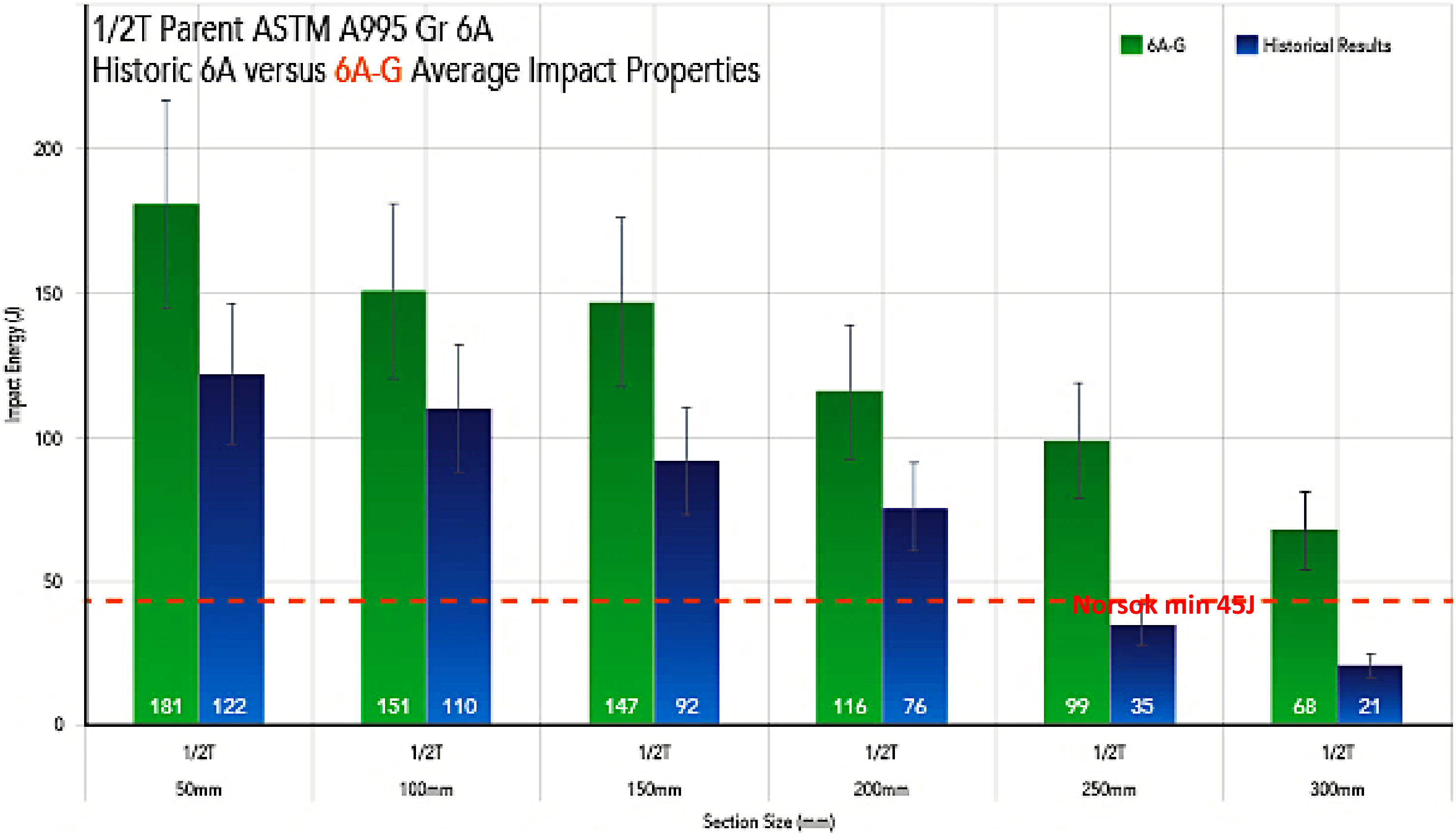
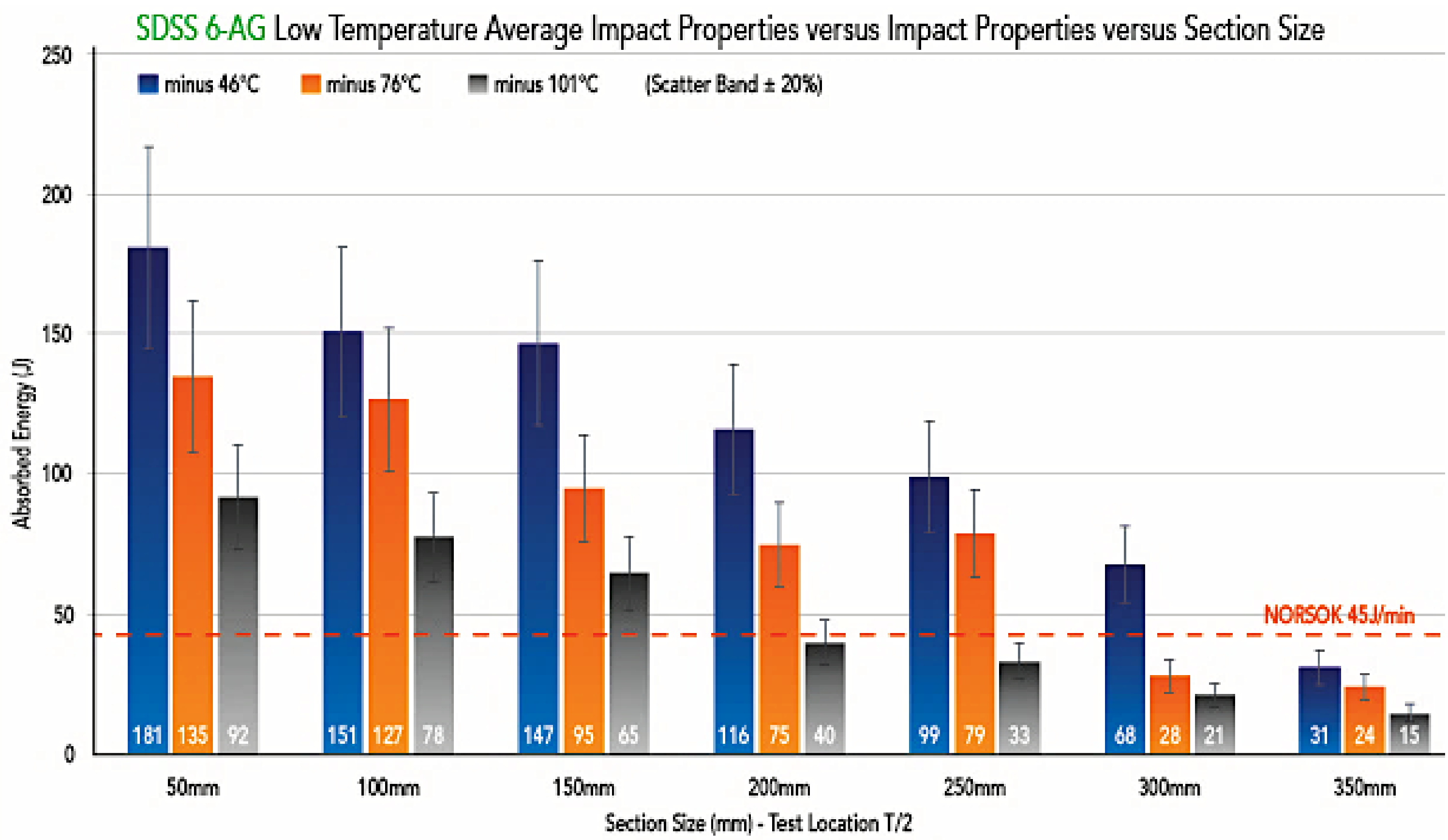


Figure 3: The very low temperature impact properties shown for 6A-G at -76°C and -101°C were not previously achievable in conventional 6A SDSS. Figure 3 shows impact properties achieved at these temperatures in a range of sections sizes in parent material 6A-G.



Parent Casting Pitting Corrosion Resistance

The autocatalytic process of pitting corrosion occurs in discrete locations on the metal surface, often starting at a surface defect, resulting in holes, pits or deep cavities **[4]**. Sigma (σ) precipitation in SDSS consumes chromium and molybdenum from the surrounding austenite and ferrite consequently reducing the corrosion resistance in those areas **[5]**. The chemical composition of the material and the pH values, temperature and chloride concentrations of the corrosion media influence performance of SDSS in such applications.

6A-G has been engineered to deliver improved pitting resistance through enhanced chemistry, reduction of intermetallic phase precipitation and metallurgical cleanliness. ASTM G48 Method 'A' and ASTM A923 method C are the standard production pitting corrosion tests, both using ferric chloride-water solution ($FeCl_3{\cdot}6H_2o$) as the corrosion media. The G48 is the most commonly specified test and for parent material SDSS the most commonly specified G48 test temperature is 50°C for duration of 24 hours.

Figure 4: Improved pitting corrosion performance at 60°C of the 6A-G parent metal versus standard 6A parent metal: G48 Method 'A'

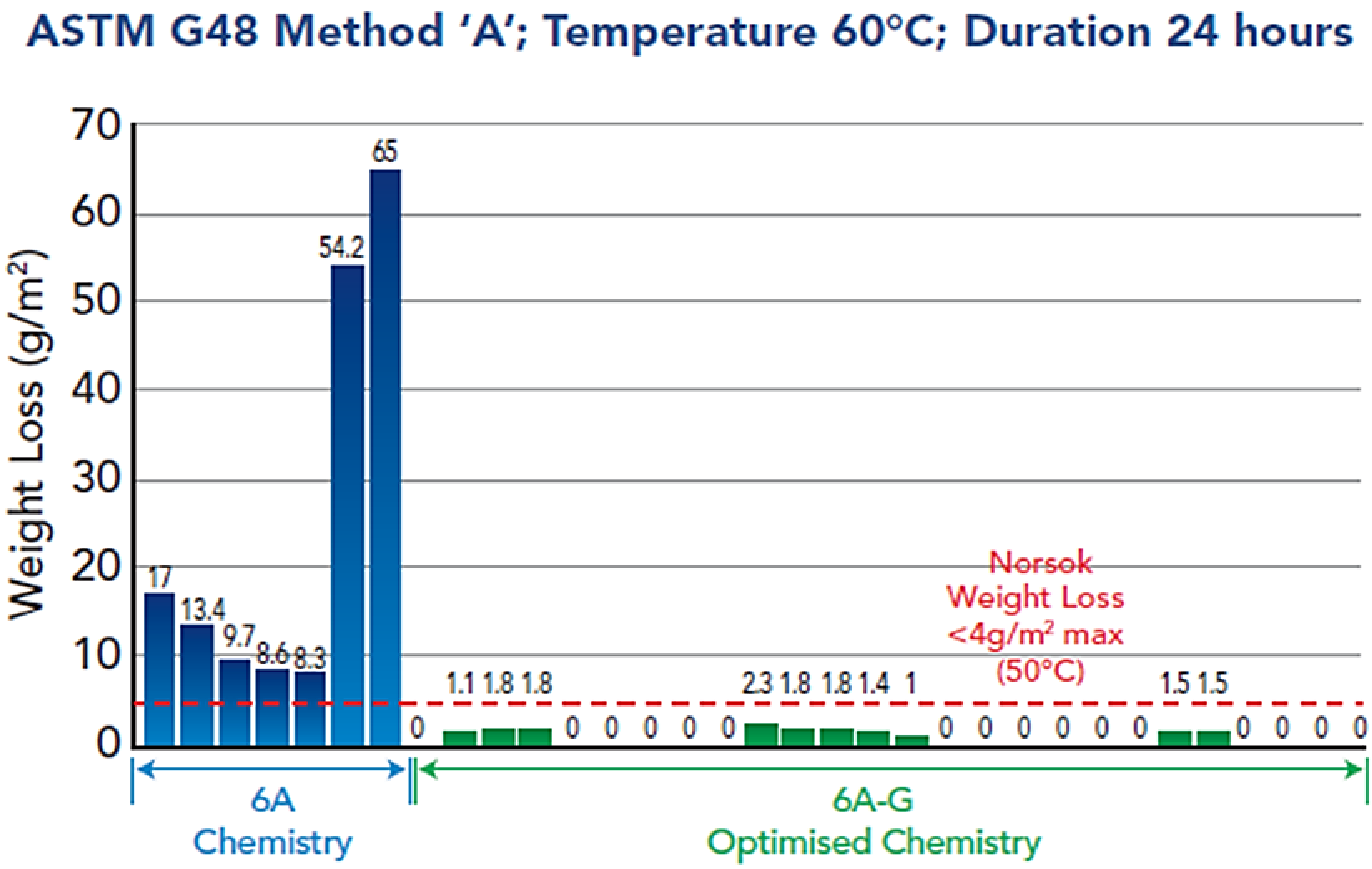


Figure 4 shows the reduced weight loss from 6A-G compared to convention 6A SDSS cast material. Test method G48 'A' was used but at an increased temperature of 60°C, rather than the standard 50°C, to demonstrate the improved resistance properties of 6A-G material. It can be seen that all 6A-G weight loss results pass by a significant margin the industry standard allowable weight loss maximum of 4g/m2, even at the increased temperature of 60°C, while all the conventional 6A cast material fails.

Super Duplex Stainless Steel Weld Metal:
ASTM A488 specifies weld qualifications for ASTM materials including an impact test location of just below the weld cap. Goodwin research showed that following post-weld heat treatment the impact results in conventional weld metal at depths greater than 35mm were unacceptable, though the parent material was unaffected. Conventional filler metals for 6A SDSS are usually either parent matching or over-alloyed with nickel. Goodwin research tested both types and table 4 details the respective chemistries of each.

Table 4: Filler composition of conventional weld material used in Goodwin research

Table 4: Conventional Filler Composition used in this trial work:

	C	Si	Mn	S	P	Ni	Cr	Cu	W	Mo	N
Filler 1	0.03	0.69	1.07	0.005	0.017	9.6	24.6	0.10	0.03	3.5	0.22
Filler 2	0.025	0.61	1.01	0.015	0.019	7.8	24.6	0.65	0.71	3.6	0.27

Research carried out on thick section welds of 100mm depth demonstrated that during post-weld heat-treatment and water-quench, sigma phase precipitated much more quickly, and to significantly deleterious levels, in the weld metal than in the parent metal. Goodwin then worked with WB Alloys to develop a filler material where sigma phase precipitated at a rate similar to the parent material during post weld heat treatment and water quench.

Figure 5: Conventional SDSS filler (left) compared with new 6A-G (right) at 100mm weld depth in the post-weld heat-treated condition.

100mm groove weld in a 200mm x 200mm x 300mm test block (PWHT condition).

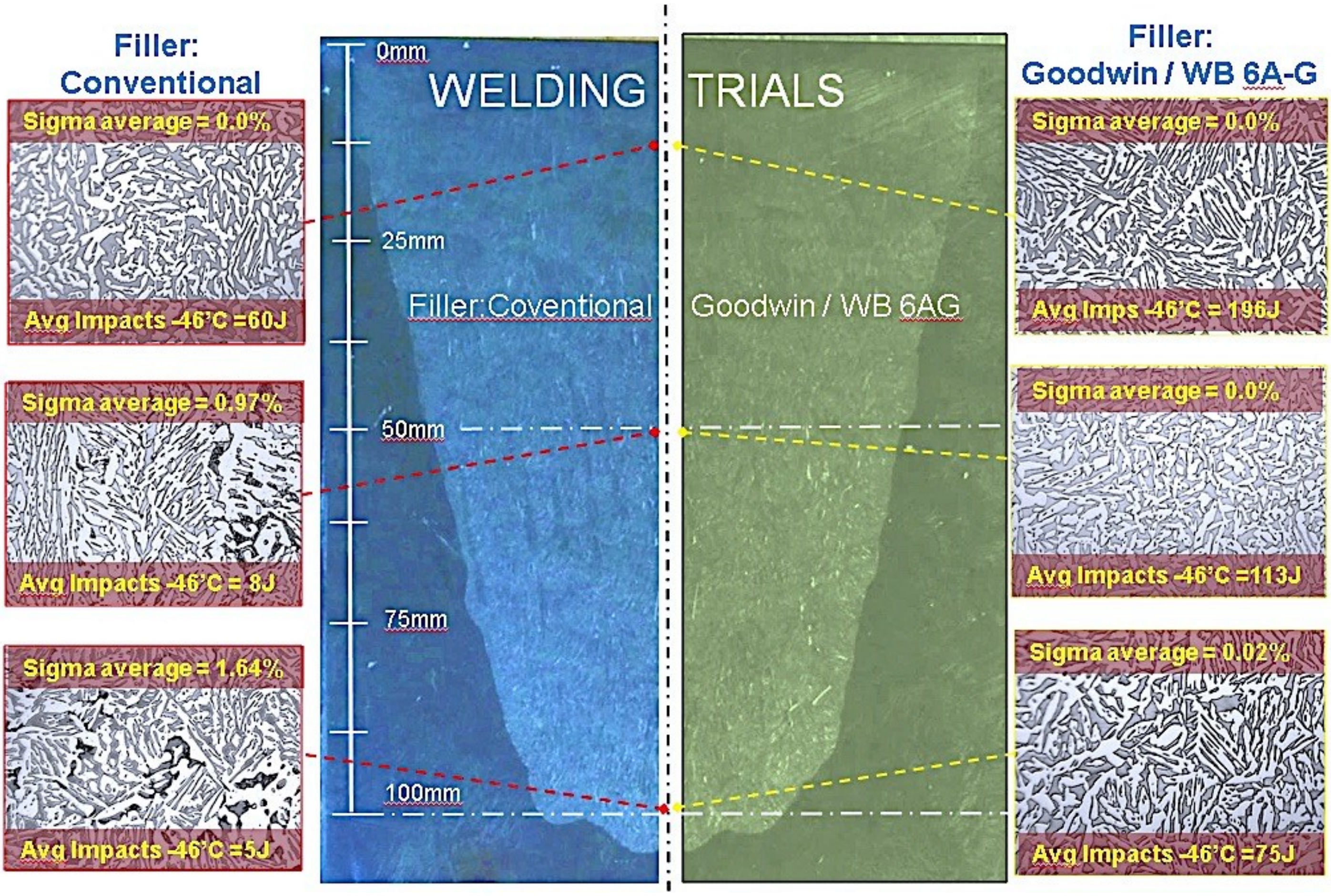


Figure 5 shows how conventional and new 6A-G filler differs in sigma precipitation at depths beneath the weld cap. At 50mm the conventional filler contained nearly 1% sigma phase, reducing impact properties to less than 10J. At the weld root the conventional filler contained over 1.5% sigma phase resulting impact values of less than 10J, contrasting markedly with the 6A-G filler which gave impact values over 1.5 times the industry standard of 45J by achieving a sigma phase level of <0.05%.

Figure 6: PWHT condition impact properties from conventional and 6A-G weld filler

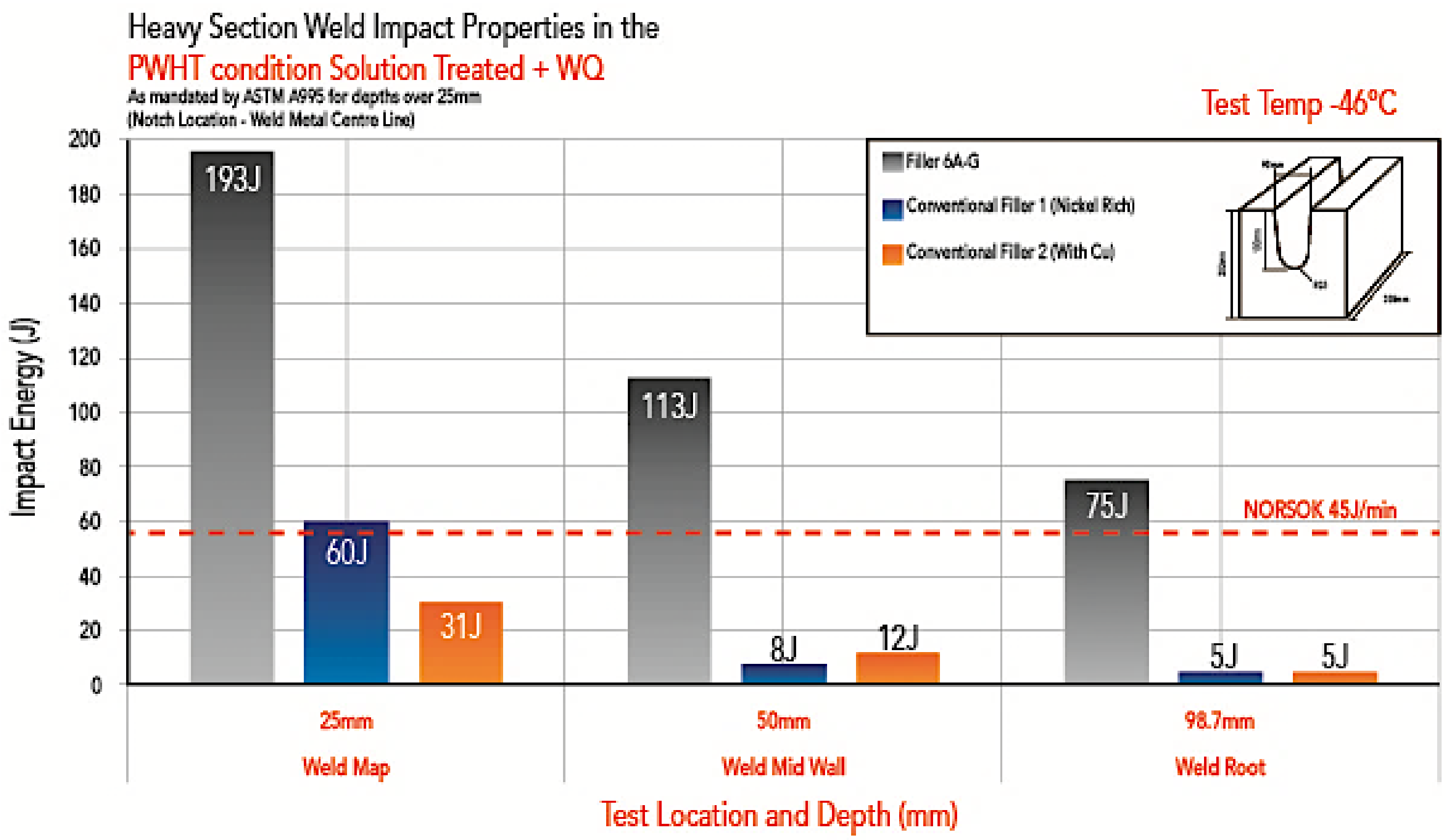


Figure 7: As-welded condition impact properties from conventional and 6A-G weld filler

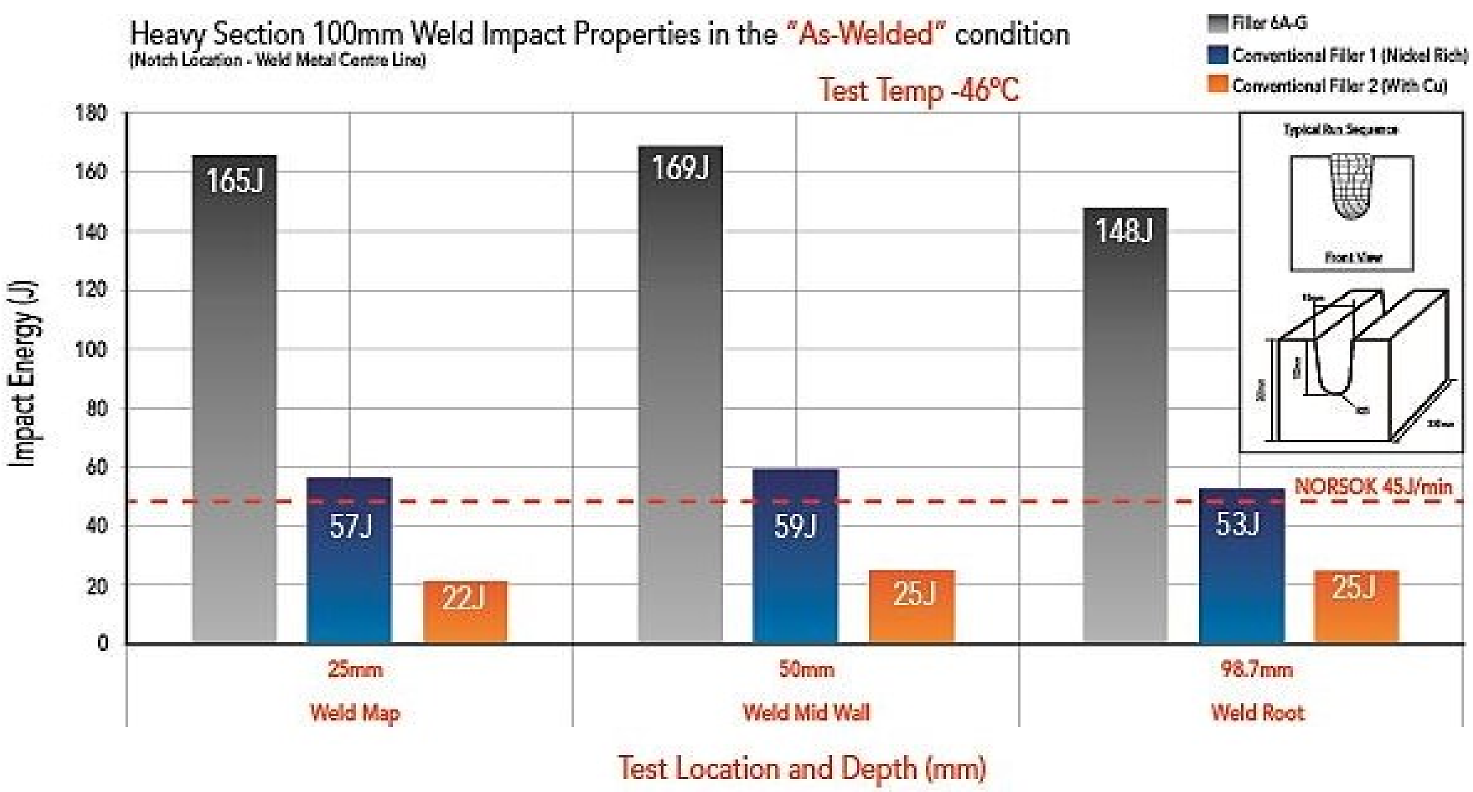


Table 5: Comparison of weld metal low temperature average impact results

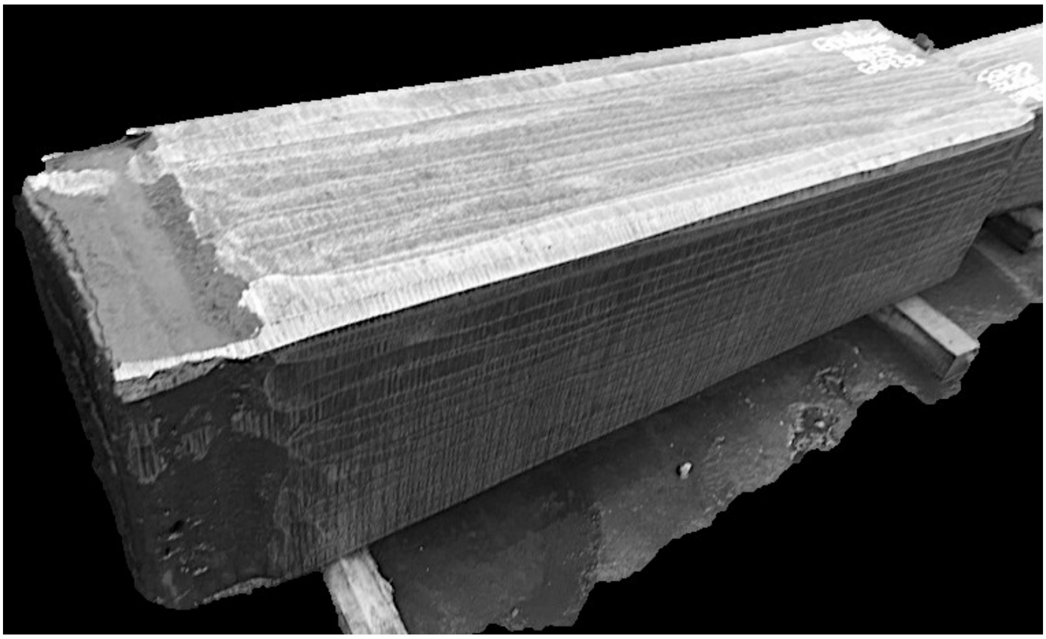
	As welded condition			Post weld heat treated condition		
Test Temperature -46°C	Avg Impacts			Avg Impacts		
Weld Test Depths	**25mm**	**50mm**	**98.7mm**	**25mm**	**50mm**	**98.7mm**
Conventional Filler 1	57J	59J	53J	60J	8J	5J
Conventional Filler 2	22J	25J	25J	31J	12J	5J
Goodwin/WB Alloys 6A-G	**165J**	**169J**	**148J**	**193J**	**113J**	**75J**

Low temperature impact properties are hugely improved in 6A-G weld filler compared to conventional filler, in both post-weld and as-welded condition, as demonstrated by figure 6 and 7 above. Microstructure cleanliness and control of sigma phase precipitation enable these improvements.

ASTM A995 Specification

The inclusion of the casting version of 6A-G into ASTM A995 is at its final ballot stage and will almost certainly be included into the specification as a set of supplementary requirements that can be specified by purchasers when superior low temperature impact properties and corrosion properties are required for the cast product. The benefit of adding the 6A-G property enhancements as a supplementary requirement in the ASTM specification is that the purchased material grade does not change, while the superior properties can be chosen when required for more arduous service requirements, greater safety, and when higher criticality is essential.

Figure 8: Shows an image of one of the first large 600mm x 600mm x 2300mm 6A-G super duplex ingots prior to forging.



Exploitation of 6A-G SDSS Enhanced Performance:
The performance advantages of 6A-G creates additional market opportunities in the following areas:

a. Applications where arctic low temperature conditions apply.

b. Desalination, oil & gas, offshore and other appliances where line temperatures are >40°C.

c. Previously testing for welds in the 'as welded' condition was limited to 40°C while for the new 6A-G material this is now 50°C and in the PWHT condition 60°C, producing an enhancement to the operational envelope.

d. Assisting the guarantee of impact resistance properties for critical applications where a margin of additional safety is required.

e. To aid the design of thicker-walled higher-pressure pumps & valves in 25% Cr super duplex with cross section up to 300mm where previous limitations have been 200mm or in some cases as low as 100mm maximum.

f. The opportunity to lower cost by substituting 6A-G in place of more nickel rich alloys such as 6%Mo austenitic steels and obtain similar corrosion resistance and much lower component weight due to the higher strength of super duplex.

Conclusions

Goodwin research has shown how deleterious phase precipitation, principally sigma (σ) phase, causes sharp and significant drop offs in the corrosion resistance and impact properties of standard SDSS. Impact properties in conventional weld filler at 50mm and 100mm depth, both in as-welded and post-weld heat-treated condition, were similarly shown to be affected.

6A-G has been developed as both parent material and weld filler and has been engineered to overcome the inherent problems in SDSS, showing significantly improved physical properties.

6A-G widens the operational scope of SDSS and improves confidence when used in existing operational parameters.

6A-G SDSS has been shown to deliver superior impact properties at -76°C at section size up to 250mm and at - 101°C at up to 100mm section size, showing it can be specified with confidence for applications at these low temperatures.

Heavy section components can be made and welded with the 6A-G weld filler and impact properties maintained at tested weld depths to 100mm, compared to the limitations of SDSS where impact properties are reduced to below industry standard at weld depths of between 25mm and 35mm in the post-weld heat-treated condition.

6A-G also shows dramatically improved corrosion characteristics in industry standard corrosion tests such as ASTM G48 method 'A' even at 60°C while standard SDSS is limited to 50°C. Weld metal using 6A-G filler now passes at 50°C and in the post welded condition at 60°C, compared to the limited performance of standard SDSS at 40°C and 50°C respectively.

Section size for SDSS has previously been limited but heavy section 6A-G can be confidently specified and successfully manufactured in section sizes up to 300mm.

The 6A-G SDSS is now commercially available in cast product forms, parent matching welding consumables and /or manufactured under license.

References:

1. *Yoon-Jun Kim,. Phase Transformations in cast duplex stainless steels, Iowa State University 2004*

2. *Topolska S,. Labanowski J, effect of microstructure on impact toughness of duplex and super duplex stainless steels. J Achiev. Mater. Manuf. Eng 2009, 36 142-149*

3. *Børvik T., Marken L.A., Langseth M., Rørvik G., Hopperstad O.S. Influence of sigma-phase precipitation on the impact behaviour of duplex stainless steel pipe fittings. Ships Offshore Struct. 2014, 1–13.*

4. *Soon-Hyeok Jeon, Soon-Tae Kim., Jun-Seob Lee, In-Sung Lee and Yong-Soo Park., Effects of Sulfur Addition on the Formation of Inclusions and the Corrosion Behavior of Super Duplex Stainless Steels in Chloride Solutions of Different pH. Dept of material Science and Engineering, Yonsei University, Soul 120-749, korea*

5. *Prabhu Paulraj, Rajnish Garg, Effect of Intermetallic Phase on Corrosion Behavior and mechanical Properties of Duplex Stainless Steel and Super Duplex Stainless Steel. Advances in Science and Technology Research Journal, Volume 9, No.27 Set 2015, pages 87-105.*

Acronyms and Abreveations:

6A-G – *Goodwin modified SDSS with enhanced impact and corrosion properties.*

SDSS – *Super Duplex Stainless Steel (Generally with a min of 24% Cr and PREN ≥40)*

ASTM - *ASTM International is an international standards organization that develops and publishes voluntary consensus technical standards for a wide range of materials, products, systems, and services.*

ASTM A995 *-Standard Specification for Castings, Austenitic-Ferritic (Duplex) Stainless Steel, for Pressure-Containing Parts.*

ASTM A890 *- Standard Specification for Castings, Iron-Chromium-Nickel-Molybdenum Corrosion-Resistant, Duplex (Austenitic/Ferritic) for General Application.*

ASTM A890/A995 Grade 6A *– a Super Duplex steel with a PRE of >40, similar grades are Zeron™ 100, UNS32760, and similar compositions are ASTM A890/995 Grade 5A.*

ASTM A488 - *Standard Practice for Steel Castings, Welding, Qualifications of Procedures and Personnel.*

As Welded – *A completed weld with no post weld heat treatment.*

PWHT *– Post Weld Heat Treatment*

$PREN_w$ *– Pitting Resistance Equivalent taking into account tungsten.*
(PRE_w = Cr + 3.3(Mo+0.5W) + 16N)

PREN *- Pitting Resistance Equivalent*
(PRE = Cr + 3.3Mo% + 16N%)

Filler – *Weld metal used in a welding process.*

ASTM G48 Method A *- Standard Test Methods for Pitting and Crevice Corrosion Resistance of Stainless Steels and Related Alloys by Use of Ferric Chloride Solution. G48 is widely used to ensure the quality of the material and resistance to pitting and crevice corrosion.*

ASTM A923 Method C - *"Standard Test Method for Detecting Detrimental Intermetallic Phase in Wrought Duplex Austenitic/Ferritic Stainless Steels".*

NORSOK M630*- "Material data sheets and element data sheets for Piping"*