# Improving Low Temperature Impact Properties & Corrosion Resistance in Super Duplex Stainless Steel Castings and Weld Metal.

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## Abstract:

Recent research and development at Goodwin has resulted in process techniques and recipes that provide very substantial increased impact properties at both standard low temperature and even lower temperatures than had previously been achievable in cast super duplex stainless steel castings and corresponding weld metal.

Previously it has not been possible in cast super duplex stainless grades such as ASTM A890/A995 grade 6A to consistently guarantee low temperature impact properties at minus 46°C above those required by the Norsok M630 specification especially in heavy sections ≥200mm.

Also, as ASTM A488 standard practice for weld qualifications for castings stipulates that impact test specimens shall be taken just under the weld cap, there had historically been little knowledge as to the low temperature impact properties in deep super duplex welds that had been post weld heat treated as mandated by the standard ASTM A995 if the weld depth was over 25mm.

This paper compares traditional ASTM A890/A995 grade 6A casting and weld metal properties with the step changing improvements achieved in the low temperature impact and corrosion properties in super duplex stainless castings (SDSS) and weld metal designated 6A-G.

## Key words:

Castings, Super Duplex Stainless Steel, ASTM A995, 6A, G48 Method A, Corrosion, Low Temperature Impact Properties, 6A-G, Weld Metal, SDSS, Norsok, M630, Sigma phase.

## Introduction:

SDSS are often specified for oil and gas industry for their corrosion, tensile and low temperature impact properties. However, these steels can suffer from the formation of deleterious phases when exposed to temperatures in the range 300°C to 1000°C during the manufacturing process, or more importantly to the manufacturer, when cooled insufficiently quickly from solution heat treatment temperatures through the same temperature range during quality and post weld heat treatment.

Unfortunately, due to this phenomena, duplex and especially SDSS have physical limitations in terms of the successfully component section sizes that can be produced. However, alternatives to large super duplex components are much more costly and complicated with long lead times, an example being nickel alloy cladding of large carbon steel valve bodies.

The slow cooling rates in SDSS heavy sections are responsible for the formation of intermetallic phases, carbides and nitrides in the centre section of the components, and in deep weld repairs leading to poor low temperature impact properties and corrosion resistance failing to meet oil & gas industry standard specifications.

Precipitation of secondary intermetallic phases in SDSS castings, forgings and weld metal in even small amounts has a dramatic effect on ductility. As little as 0.1% Sigma phase (σ), can start to reduce properties, and values of 1% can reduce impact values by 60% to 70% with an equally rapid reduction in corrosion properties.

This has resulted in reservations within the oil and gas industry for the use of large section super duplex steels components due to the risk of poor centre section properties. However, what should be of at least equal concern, determined by Goodwin development work, is the precipitation of intermetallic phases in the weld repairs in heavy sections after specified post weld heat treatment.

This paper describes the step change improvements of properties achieved in the parent cast and weld metal when very specific chemistry and process parameters are observed in the manufacture of product. This development work has resulted in the reduction of the section size limitations of SDSS castings and welds, and the vast improvement in corrosion and impact properties of both heavy and thin section castings.

**Key step change benefits are of 6A-G are:**

- Vastly enhanced low temperature impact properties in parent cast & weld material. Enabling a greater level of confidence when producing SDSS castings and welds with regards to manufacturing variables.

- Low temperature impact properties tested at -46ºC are up to150% higher than the Norsok minimum and acceptable impact properties (45J Av / 35J Min) at -101°C are achieved.

- Crucially enables heavier sections to be successfully produced while maintaining excellent impact strength and corrosion performance in centre sections.

## Compositions:

Generic chemical compositions for super duplex casting grade ASTM A890/A995 Grade 6A is detailed below.

| | 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 | 25.0 | 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 |

**PREN = %Cr + 3.3x%Mo + 16x%N ≥ 40*

## How does it work?

Alloy 6A-G has its own special chemistry that provides the enhanced technical performance. This is achieved by having a far more stringent chemistry than required by conventional specifications. The fundamental difference is the much lower levels of sigma (σ), and other deleterious secondary phases in section sizes, where in conventional 25% Cr SDSS grades a certain percentage of sigma phase may be expected, and it does require a significant amount of sigma phase to degrade the impact properties [8].

For thicker sections with the conventional super duplex grades, values of 1% or more sigma phase can be expected in the very centre position while for alloy 6A-G in section sizes ≤200mm, sigma phase will typically be <0.02%. For sections 250mm to 300mm <0.5% can be expected for an equivalent cooling rate constant.

## Low Temperature Impact Property Improvements:

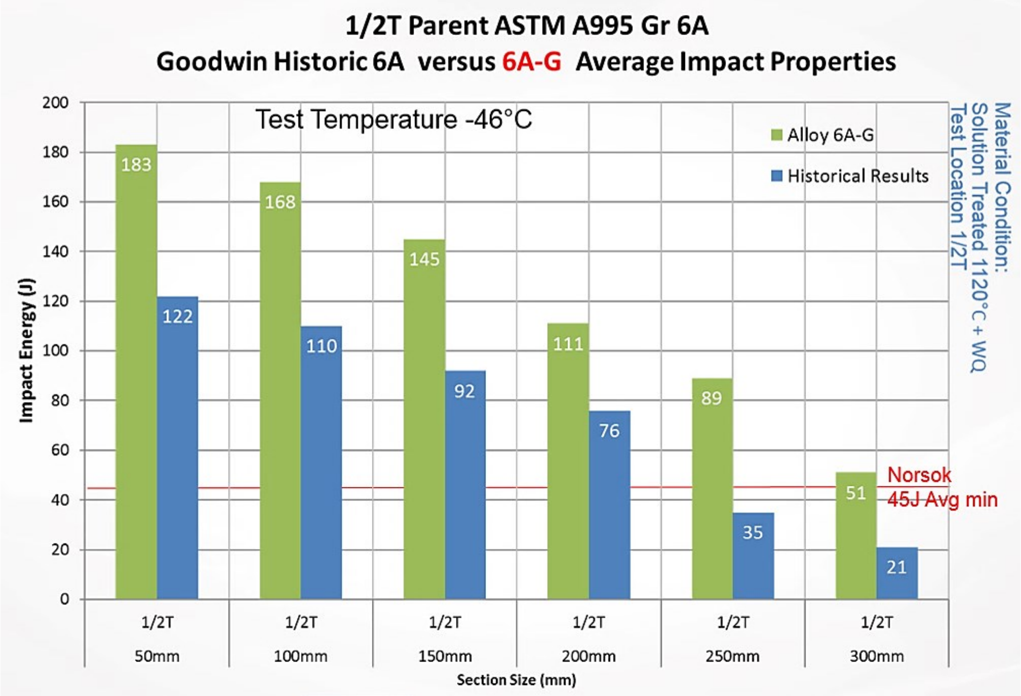


**Figure 1:** Impact properties of 6A-G SDSS compared with conventional 6A SDSS over a range of section sizes from 50mm through to 300mm

Figure 1 shows the average impact improvements that are achieved (green bars) over conventional 6A SDSS (blue bars) taken from Goodwin database using secondary AOD refinement or remelting of AOD refined material.

The blue values from the conventional material give the impression that the Norsok specification minimum average requirements of 45Joules average can be achieved in sections up to 200mm. However, this figure has to be considered in conjunction with the negative 20% scatter band (detailed in figure 2). This shows that it is possible to obtain values lower than the mean, and taking this into account the limit for guaranteed low temperature impact properties is restricted to 200mm to meet the 45J Norsok min requirements, and for other Oil and Gas industry minimum requirements of 60J average, then the maximum section that can be guaranteed is only 150mm.

However, the limit for 6A-G material is 300mm to meet 45J average, and 250mm to guarantee to achieve the heightened oil industry specification of 60J average.

| TABLE 1 | Section Size (1/2T location) | | | | | |
|---|---|---|---|---|---|---|
| **Material** | **50mm** | **100mm** | **150mm** | **200mm** | **250mm** | **300mm** |
| units | Av (J) | Av (J) | Av (J) | Av (J) | Av (J) | Av (J) |
| Mean 6A SDSS | 124 | 110 | 85 | 65 | 39* | 21* |
| -20% Scatter | 92.4 | 88 | 68 | 52** | 31.2* | 16.8* |
| Mean 6A-G SDSS | 190 | 165 | 139 | 111 | 84 | 60 |
| -20% Scatter Band | 152 | 132 | 111.2 | 89 | 67.2 | 48 |
| | Improvements over conventional 6A Duplex | | | | | |
| Mean Δ | +66J | +55J | +54J | +46J | +45J | +38J |
| -20% Scatter Band Δ | +59J | +44J | +43J | +37J | +36J | +30J |

**Table 1:** Impact properties versus section size and -20% Scatter Band

**These values do not meet impact minimum value requirements for Norsok (45J avg min)*

***The -20% scatter band result does not meet the oil industry heightened specification of 60J avg min.*

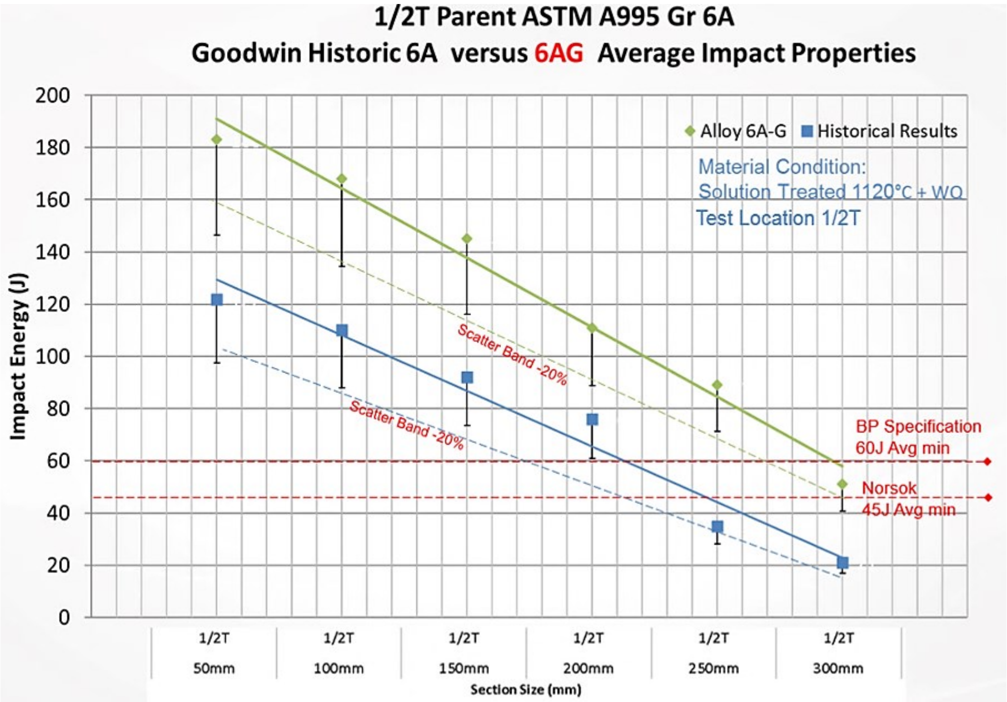


**Figure 2:** shows the negative 20% scatter band for both the mean 6A-G and conventional 6A SDSS.

Figure 2 shows that with conventional 6A duplex steel it is not possible to guarantee impacts values meeting the oil industry heightened specification of 60J average in a 200mm section and to the contrary, the safey margin is so great with the 6-AG material, the oil industry higher specification can be achieved with ease at 200mm and even at 250mm, which is a step changing improvement in impact properties of thick section SDSS castings.

It should be noted that a few manufacturers have claimed achievable Norosk complient impact test results being obtained in section of 280mm for ASTM A890/995 5A and 6A grades. However, achieving a single set of results from single test item heat treatments have to be treated with caution with regards to whether these values can consistenly be achieved in a production scale enviroment, when multiple casting are heat treated and quench heat transfer is less efficient.

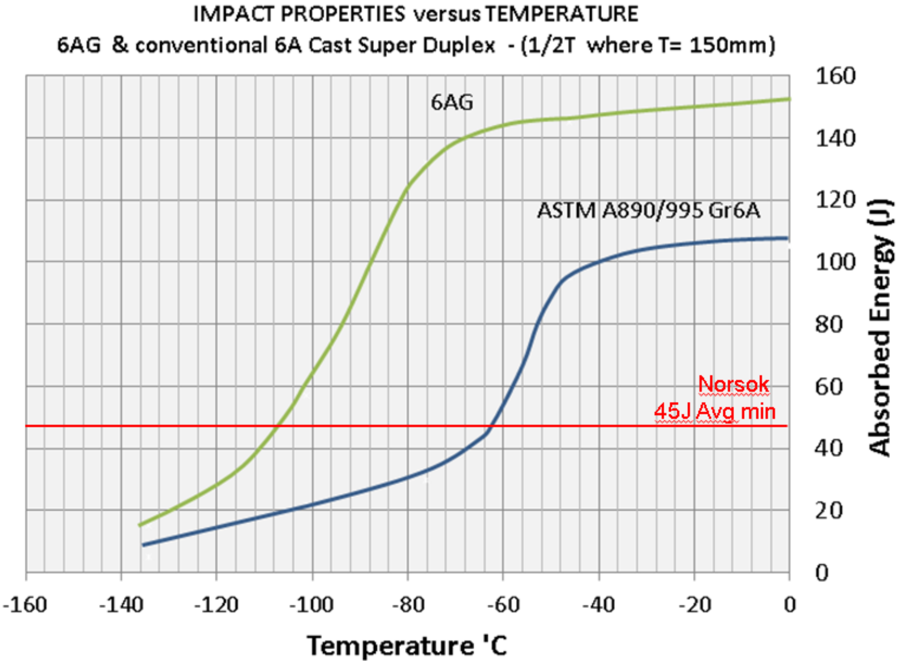


**Figure 3:** 6A-G versus conventional 6A Transition Curve

Figure 3 shows the transition curve for 6A-G compared with conventional 6A duplex samples taken from testing of 150mm test blocks. The transition cure for conventional 6A falls below the minimum Norsok M630 impact requirement specification at -60°C, while the 6A-G SDSS meets the specification minimum at -103°C. This is a clear -43°C advantage in low temperature ductility and potentially allows for the material to operate in lower temperature environments, or giving a much greater confidence in impact resistance especially when heavy sections are specified.

Figure 4 shows impact test data for 6A-G SDSS tested at a variety of test temperatures and section sizes. Test section location was at 1/2T taken from Norsok compliant sized test block.

**Impact Properties of 6A-G**
**(Test Temperature versus Section Size)**

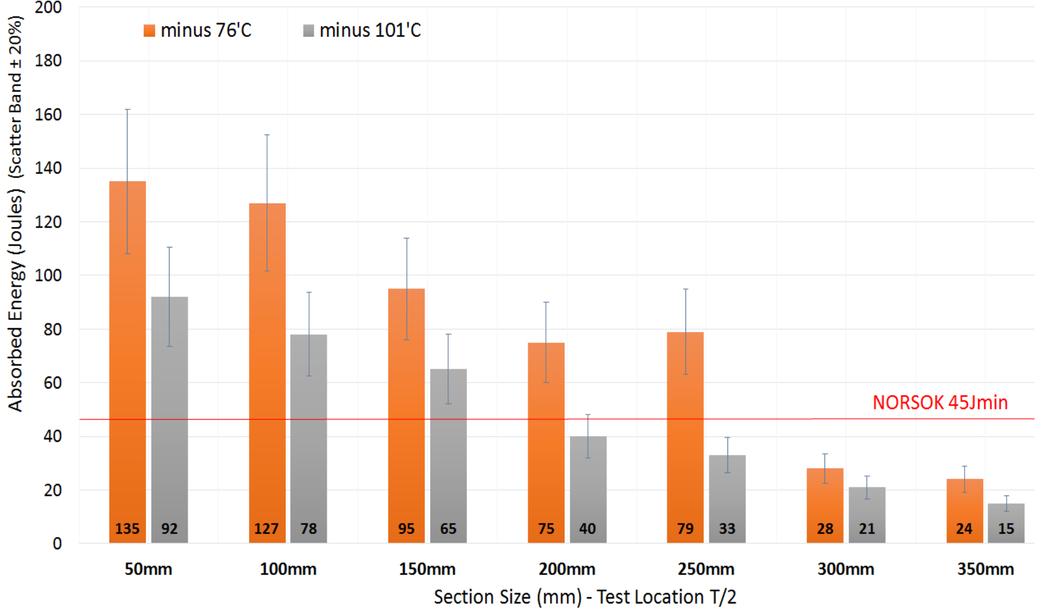


**Figure 4:** 6A-G Impact testing at ,-76°C and -101°C over a range of section sizes

**Through Section Tensile Properties:**

An excellent characteristic of SSDS is the consistent tensile properties achieved during through section testing. No discernable drop off in ultimate tensile strength or proof stress is evident as section size increases, unlike conventional normalized or quench and tempered carbon and low alloy steels.

| **TABLE 2** Section Size (mm) | Mat-erial | UTS (N/mm$^2$) | 0.2% Proof Stress (N/mm$^2$) | Elongation (%) | Reduction of Area (%) | Hardness (BHN) |
|---|---|---|---|---|---|---|
| | **ASTM Spec** | **680**N/mm$^2$ **min** | **450**N/mm$^2$ **min** | **22% min** | **35% min** | **350 BHN max** |
| 50mm | 6A-G | 775 | 501 | 43 | 61 | 245 |
| 150mm | 6A-G | 765 | 485 | 37 | 62 | 232 |
| 200mm | 6A-G | 756 | 495 | 35 | 60 | 234 |
| 250mm | 6A-G | 750 | 488 | 38 | 64 | 234 |
| 300mm | 6A-G | 752 | 492 | 38 | 47 | 234 |

Material condition: 1120°C solution treatment followed by rapid water quench
Test Location for all sections sizes: 1/2T

**Table 2:** Through section tensile properties of 6A-G SDSS

Table 2 details the average tensile test data of twelve heats of 6A-G SSDS tested over a range of section sizes from 50mm through to 300mm section.

| **TABLE 3** Section Size (mm) | Mat-erial | UTS (N/mm$^2$) | 0.2% Proof Stress (N/mm$^2$) | Elongation (%) | Reduction of Area (%) | Hardness (BHN) |
|---|---|---|---|---|---|---|
| | **ASTM Spec** | **680**N/mm$^2$ **min** | **450**N/mm$^2$ **min** | **22% min** | **35% min** | **350 BHN max** |
| 50mm | 6A | 765 | 490 | 38 | 68 | 229 |
| 150mm | 6A | 746 | 474 | 35 | 59 | 229 |
| 200mm | 6A | 718 | 472 | 31 | 55 | 226 |
| 250mm | 6A | 761 | 468 | 25 | 46 | 234 |
| 300mm | 6A | 712 | 482 | 18 | 12 | 255 |

Material condition: 1120°C solution treatment followed by rapid water quench
Test Location for all sections sizes: 1/2T.

**Table 3:** Through section tensile properties of conventional 6A SDSS

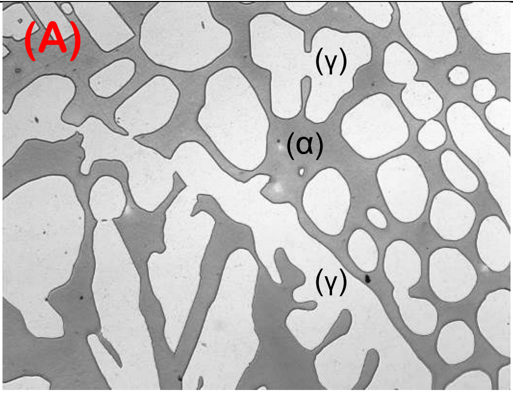
Table 3 shows the tensile data for conventional cast 6A SDSS. Values for elongation and ductility are comparable up to 200mm, thereafter in sections 250mm and 300mm the elongation and reduction in area values reduce much more than the 6A-G material, due to the formation of intermetallics which increase hardness [8] and effect ductility. Fig 5 shows results of testing of metallography testing at the 1/2T location of varying section sizes of 6A-G SDSS.

Figure 5 shows metallography of 6A-G section sizes 150mm through to 300mm. All micrographs show “clean” microstructures with approximate 45% ferrite (α) and 55% austenite. The figure clearly shows the sigma phase precipitation in the 6-AG material in section sizes up to 300mm is very low (i.e. ≤0.35%), this was calculated using a grid method similar to that used for ferrite calculation.

**Fig 5: Metallography:** (Etchants NaOH electrolytic; **(All magnifications x100)**

### 6A-G 1/2T Location 150mm Section

**0.0% Sigma Phase, (avg impacts 145J)**



### Microstructure Evaluation

**Test Temperature: -46°C**

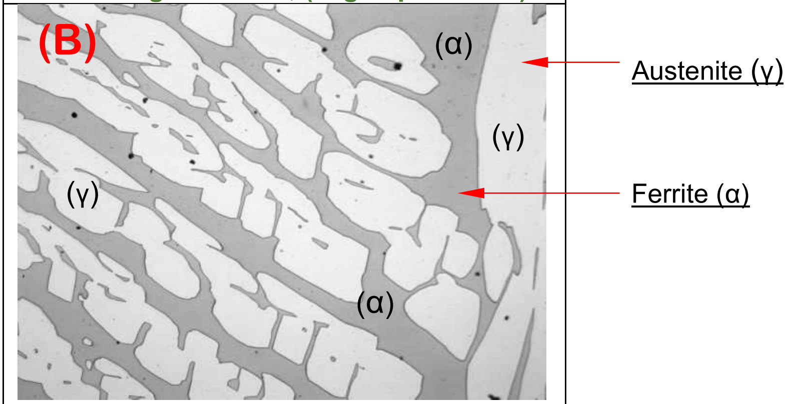
Microstructures consist of light pools of austenite (γ) within a ferritic(α) matrix with low % of sigma (σ)

| Section | Ferrite (α) | Austenite (γ) | Sigma (σ) |
|---|---|---|---|
| (A) 150mm | 45 | 55 | 0.0 |
| (B) 250mm | 44 | 55.7 | 0.25 |
| (C) 300mm | 46 | 53.6 | <0.35 |

All micrographs between 150mm and 300mm with <0.4% sigma phase

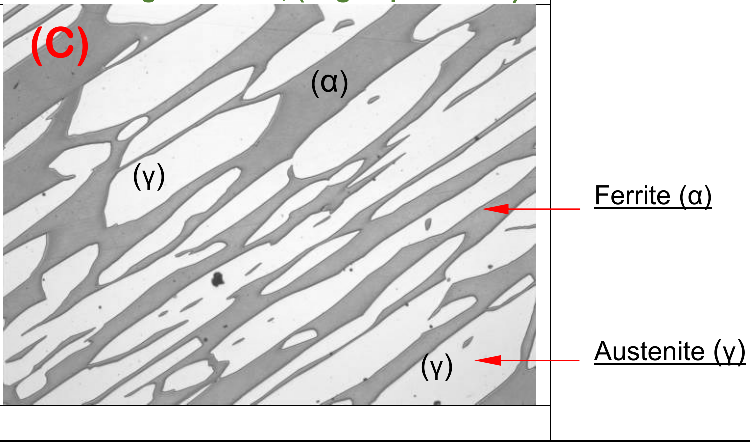
### 6A-G 1/2T Location 250mm Section

**0.25% Sigma Phase, (avg impacts 89J)**



### 6A-G 1/2T Location 300mm Section

**<0.35% Sigma Phase, (avg impacts 51J)**



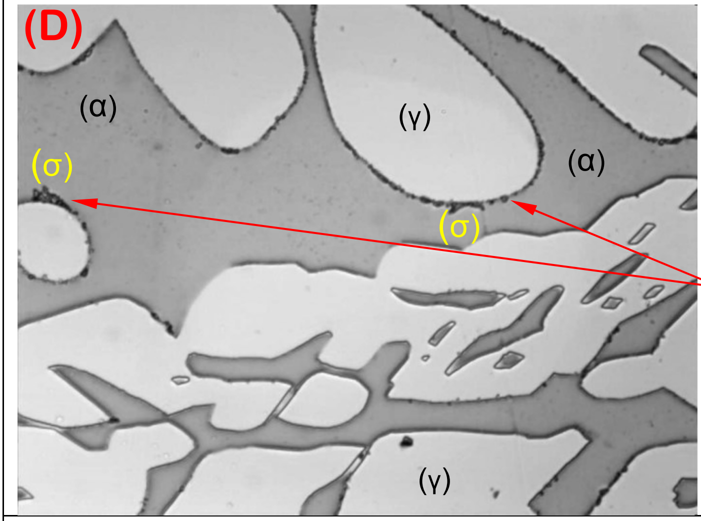
| **Fig 6: 6A-G 1/2T Location 350mm Section x500** | **Comments** |
|---|---|
|  | Microstructure shows light pools of austenite (γ) within a ferritic (α) matrix.<br>Phase balance is approximately 45 to 50% ferrite.<br>Sigma phase (σ) (dark) Precipitated initially on the (γ)/ (α) interfaces.<br>Approx. sigma (σ) < 1.0% |
| Etchants NaOH electrolytic (avg Impact 30J) | |

Fig 7 shows the relationship between %sigma (σ) phase on average low temperature impact resistance for cast ASTM A890/A995 6A and conventional 2507 over alloyed weld metal filler in the PWHT condition. This graph was developed during the course of the experimental work within this paper. Sigma phase is a Cr-Mo rich hard precipitate which occurs at temperatures between 600-1000 °C [2, 3].

At temperature between 850-900 °C, sigma phase has its fastest precipitation rate. Sigma phase precipitation starts at α/α boundaries and α/γ boundaries as they are found to be high energy nucleation sites [1]. Later, Sigma phase grows in the ferrite phase as the diffusion rate in ferrite phase is 100 times faster than that of austenite, which also makes it a favourable site for precipitation of all intermetallic phases [2] [7]. Figure 6 shows the precipitation of the sigma phase initiation at the α/γ boundaries of a 350mm section of 6A-G material. Noteworthy is that only the initiation of sigma precipitation has occurred, and not second stage growth which consumes quickly into the ferrite pools.

Topolska & Labanowski [4] claimed that the maximum allowable sigma phase content in wrought SDSS was 8%. This value corresponds to critical impact energy value of 27 J in Industrial applications. However, since 2009, generally the low temperature impact requirements for SDSS are 45J or 60J.

Similar observations were made to evaluate maximum allowable sigma phase content in SDSS pipe fittings in subsea applications [5]. The authors claimed that up to 5% sigma phase content is allowable.

Investigation at Goodwin in cast and weld metals show that sigma (σ) phase values much less than 5% to 8% cause SDSS impact values tested at -46°C to result in values less than industry specification of 35J single/ 45J average, and sigma values as little as 1.5% to 2% can result in single figure impact values (see figure 7).

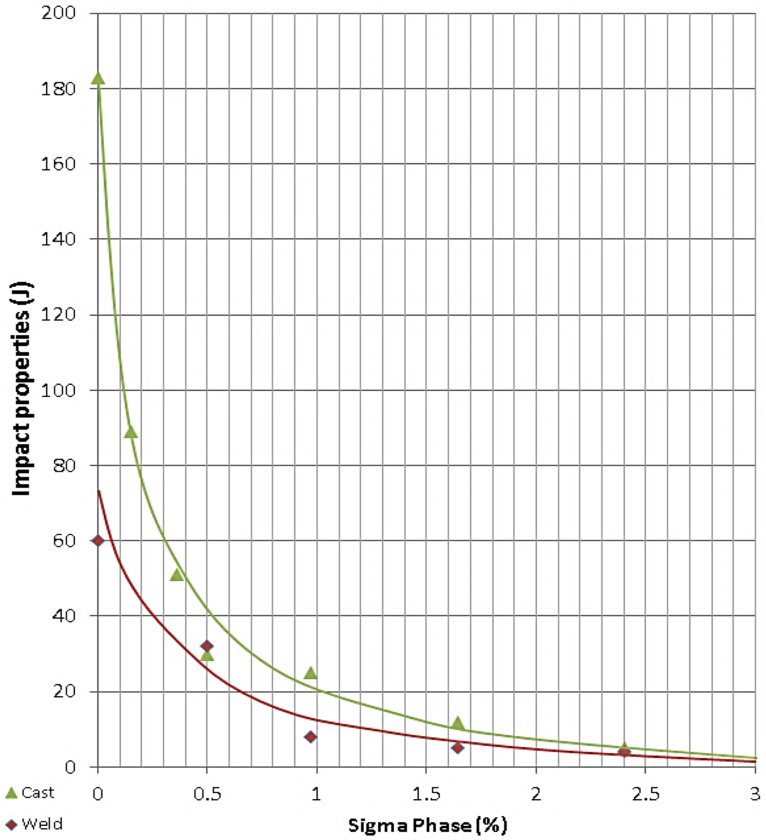


**Figure 7:** Shows the effect of Sigma (σ) Phase on cast ASTM A890/A995 6A and conventional 2507 over alloyed weld metal in the PWHT condition.

## Parent Casting Pitting Corrosion Resistance

Pitting corrosion is an autocatalytic process and is a localised phenomenon which leads to formation of small pits or holes on metal surface. It can be initiated at a surface defect [10] which leads to formation of deep cavities in the metal. SDSS are susceptible to pitting corrosion depending on the chemical composition of material, chloride concentrations, pH value and temperature of the corrosion media. Sigma (σ) phase is rich in Cr and Mo content and the precipitation of σ phase causes consumption of Cr and Mo from surrounding ferrite and austenite, which leads to reduction in corrosion resistance of SDSS. [1] The 6A-G material has improved pitting resistance due to its enhanced chemistry, cleanliness, and reduction of intermetallic phase precipitation. Two standard corrosion tests are used in the routine production testing of SDSS, ASTM G48 Method A and ASTM A923 method C, the former being the more commonly stipulated. Both tests use ferric chloride mixed with water (10% $Fe3Cl\cdot 6H2O$) as the corrosion media, and for parent material SSDS the G48 test temperature normally stipulated is 50°C with a duration of 24hrs.

**Figure 8:** Shows an SEM view of a pit initiation site after 5hrs, and 10hrs at 50°C – G48 Method A in SDSS. The initiation site is associated with a cluster of inclusions within the metal matrix.

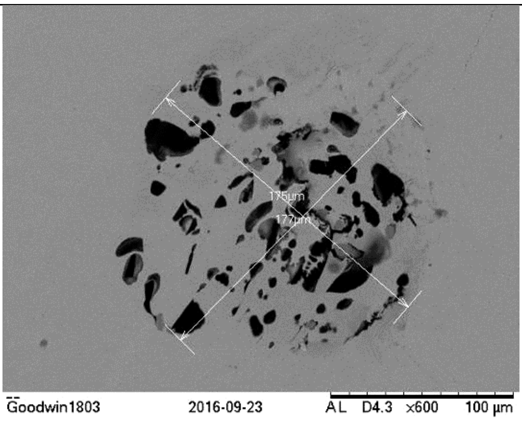
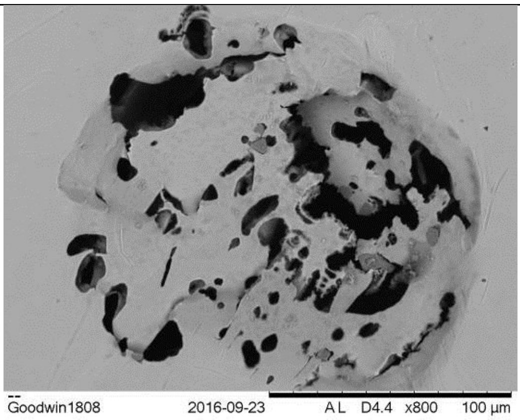
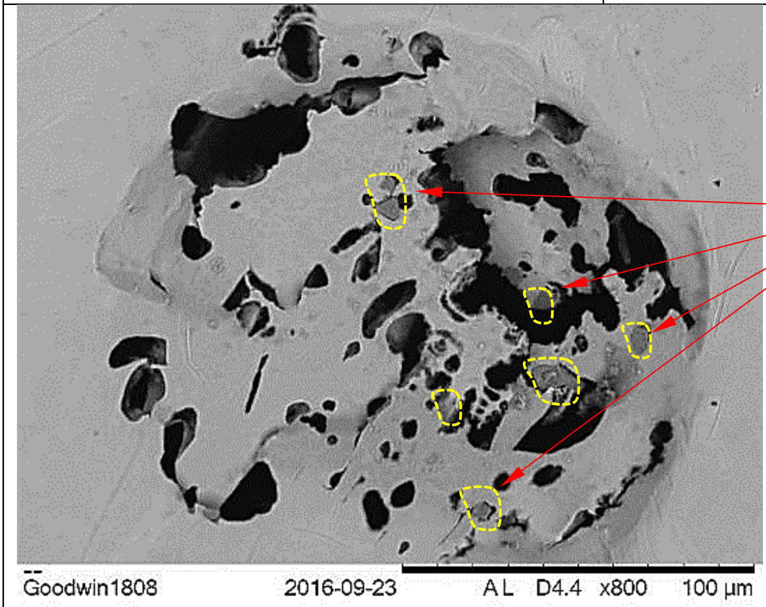
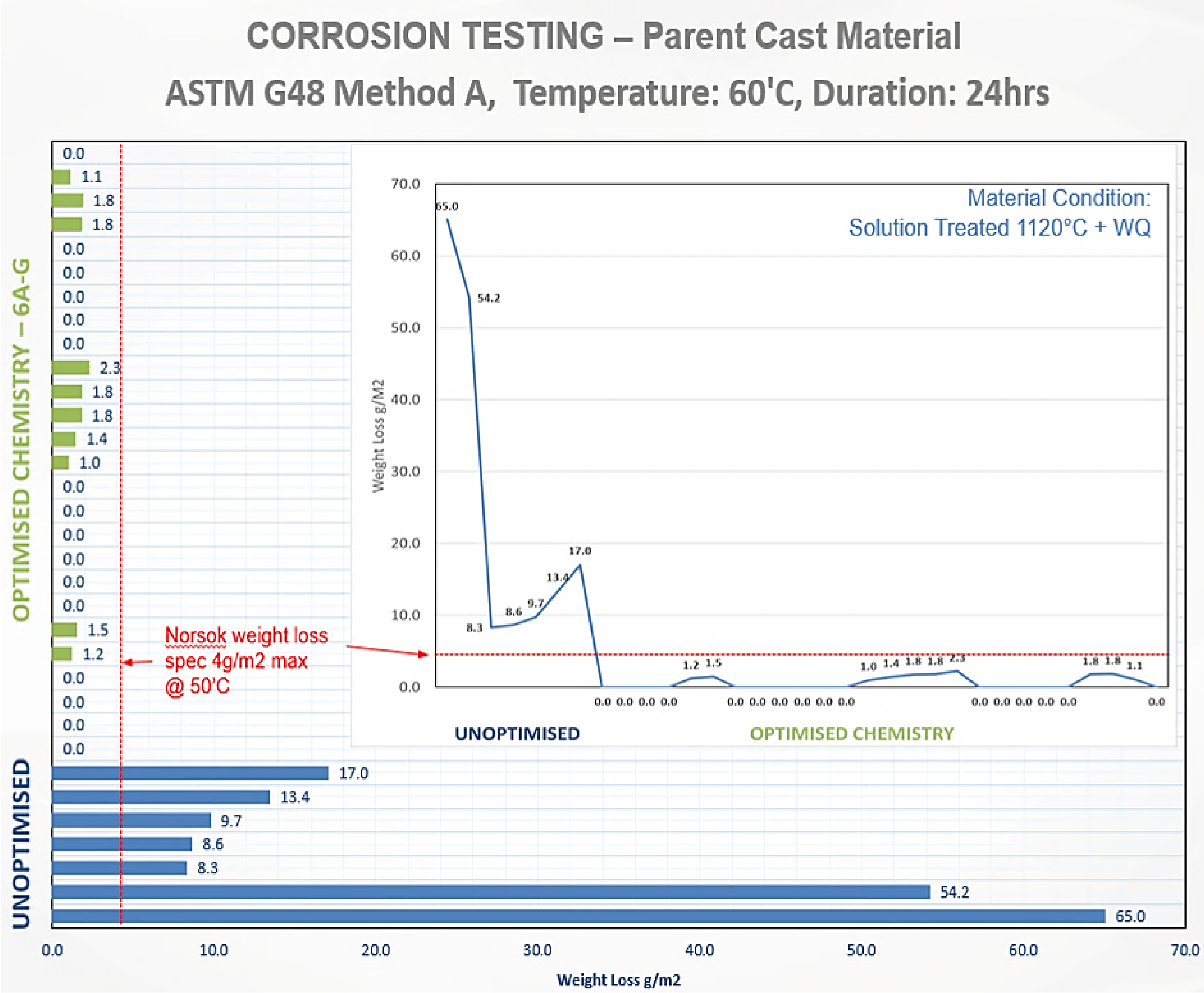
| **G48 Method A - 5hrs at 50°C (x600)** | **G48 Method A – 10hrs at 50°C (x800)** |
|---|---|
|  |  |
|  | MnS inclusion cluster.<br>Pitting attack initiates at the inclusion /metal interface. |

Fig. 9 shows the comparison between the weight losses of 6A-G SSDS compared with the weight loss of conventional 6A SDSS cast material during G48 method A testing at 60°C. This temperature was selected to test the material beyond the standard test regime of 50°C to demonstrate the enhanced resistance capable with the 6-AG material. The industry standard maximum allowable weight loss is 4g/$m^2$, figure 9 demonstrates that all 6A-G heats have a weight loss less than the maximum allowable for 50°C, but is achieving this at 60°C, while the conventional 6A cast material heats all fail to pass the weight loss restriction by a large margin. Goodwin has also pass data for 6A-G heats at both 65°C and 70°C not presented in this paper but worthy of note at this time.


CORROSION TESTING – Parent Cast Material

ASTM G48 Method A, Temperature: 60'C, Duration: 24hrs

## Super Duplex Steel Filler Metal

Goodwin research and development on SSDS weld metal originally focussed on deep welds in SDSS castings. This work lead to the fundamental discovery that weld in excess of 35mm in heavy sections which subsequently required a solution heat treatment resulted in the reduction of impact properties of the weld metal when using conventional commercial fillers, while the parent material was unaffected.

Commercial fillers for 6A super duplex parent material are generally split into two groups, parent matching or over alloyed. During our testing regime, both types of consumable were tested. Upon investigation on multiple thick section mock tests it was discovered that the conventional weld metal responded differently to the parent material during post weld heat treatment and began to precipitate sigma (σ) phase much more quickly than the parent material during quenching from post heat treatment temperatures.

### Comparison of Sigma Precipitation Rates in Weld Metal versus Cast Metal

Figure 10 shows the difference in isothermal sigma phase precipitation in SDSS weld metal compared with SDSS cast metal at 875°C.The graph was created from small scale testing performed by Goodwin, and shows the precipitation of sigma phase in weld metal is much quicker than in cast metal up to 10mins and has to be taken into consideration when weld repairing castings or fabrication of forgings/ pipes requiring PWHT.

The hypothesis for the difference in precipitation kinetics could be a function of the coarseness of the cast microstructure compared with the very fine weld microstructure. As sigma phase is a function of diffusion, its likely the distances between microstructural constituents causes the differences in precipitation rates.

This presented much less of a problem if the weld could be left in the as welded condition, but where specifications call for a more mandatory PWHT this created at the time an insurmountable problem with current commercially available filler metals. This constituted an urgent necessity to develop a filler material that had a quench response with regards to intermetallic precipitation kinetics much closer to that of the parent material.

**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 |

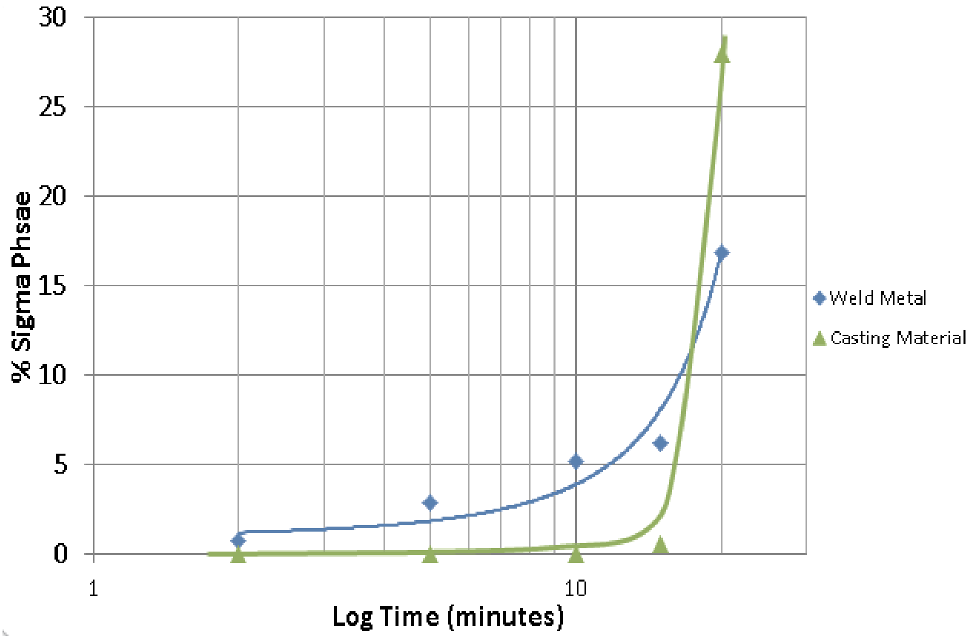
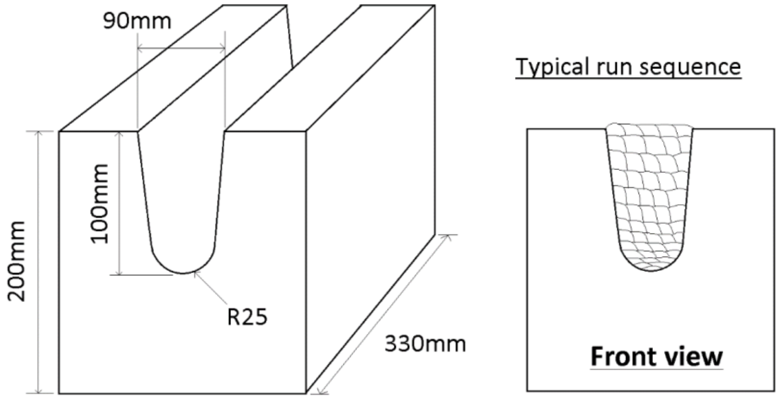


**Figure 10:** Comparison of isothermal sigma formation for SDSS parent Matching weld metal and cast material at 875°C.

**Figure 11:** Details the dimensions of the weld test blocks used in the deep welding trials, where the block constitutes a considerable thermal mass when performing post heat treatment.



Weld metal deposit depth was 100mm and strict weld procedural parameters maintained, monitored and third party witnessed during welding. Inter-pass temperature and heat input was strictly controlled for all weld fillers trialled to maintain consistency.

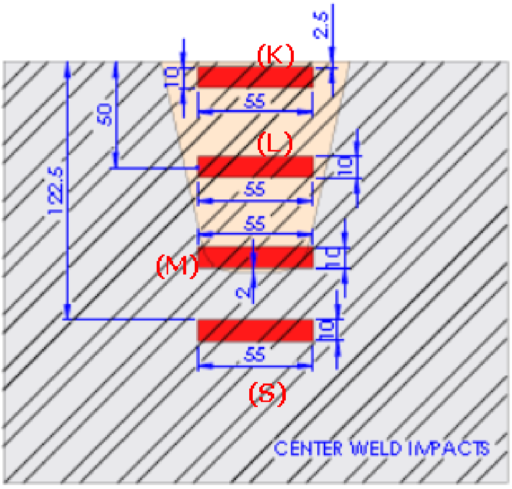


**Fig 12:** Details the position of the impact samples produced from each 200mm test block.

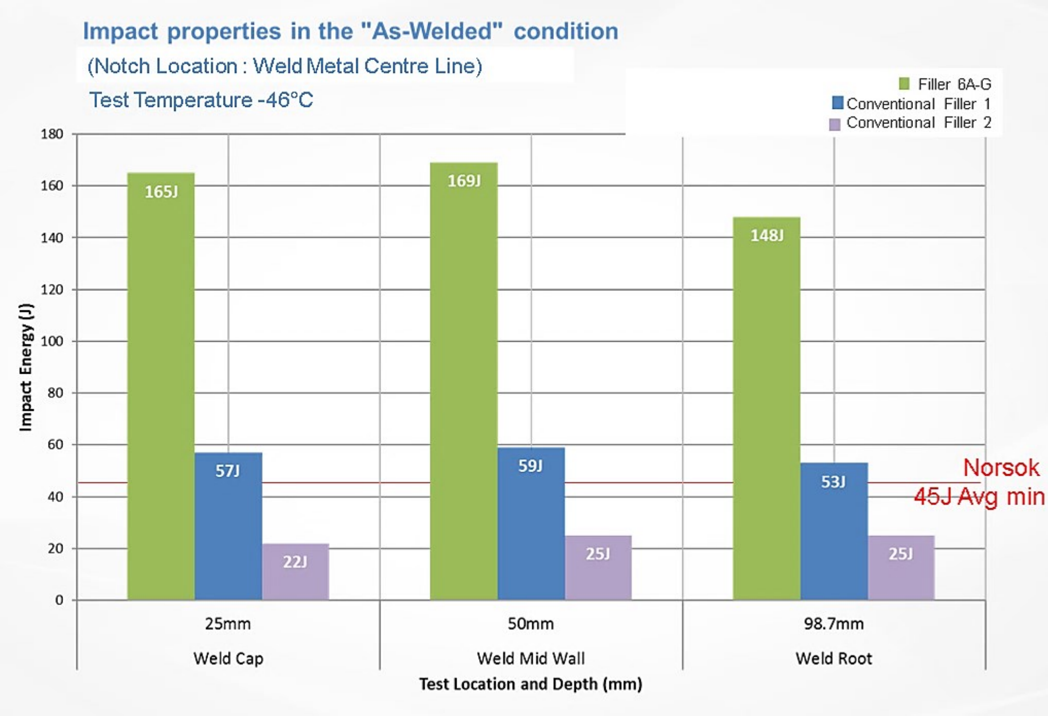


**Figure 13:** Conventional Fillers (1 &2) compared with 6A-G in the as welded condition.

Fig 13 shows the marked improvement in as welded properties using the 6A-G filler metal compared with standard parent matching and over alloyed with nickel welding consumables.

| Filler | Weld Depth | | |
|---|---|---|---|
| **Conventional Filler (1)** | **25mm** | **50mm** | **100mm** |
| Ferrite(α) | 35% to 50% | | |
| Sigma(σ) | 0.0% | 0.0% | 0.025% |
| Avg Impact -46°C | 57J | 59J | 53J |
| **Conventional Filler (2)** | **25mm** | **50mm** | **100mm** |
| Ferrite(α) | 35% to 50% | | |
| Sigma(σ) | 0.0% | 0.01% | 0.0% |
| Avg Impact -46°C | 22J* | 25J* | 25J* |
| **Filler** | **Weld Depth** | | |
| **6-AG** | **25mm** | **50mm** | **100mm** |
| Ferrite(α) | 37% to 46% | | |
| Sigma(σ) | 0.0% | 0.0% | 0.01% |
| Avg Impact -46°C | 165J | 169J | 148J |

**Table 5:** Summary of weld metal, impact properties and sigma (σ) %
in the as welded condition. The results of this table are shown graphically in figure 13 and plotted against the Norsok min average specification of 45J.

| **Filler** | **Weld Depth** | | |
|---|---|---|---|
| **Conventional 1** | **25mm** | **50mm** | **100mm** |
| Ferrite(α) | 37.5% to 50% | | |
| Sigma(σ) | 0.0% | 0.97% | 1.64% |
| Avg Impact -46°C | 60J | 8J* | 5J* |
| **Conventional 2** | **25mm** | **50mm** | **100mm** |
| Ferrite(α) | 35.7% to 50% | | |
| Sigma(σ) | 0.0% | 1.51% | 1.85% |
| Avg Impact -46°C | 31J* | 12J* | 5J* |
| **Filler** | **Weld Depth** | | |
| **6-AG** | **25mm** | **50mm** | **100mm** |
| Ferrite(α) | 40.3% to 46% | | |
| Sigma(σ) | 0.0% | 0.0% | 0.02% |
| Avg Impact -46°C | 199J | 113J | 75J |
| Avg Impacts -96°C | 134J | 119J | 85J |

*Values are less than specified by industry specifications.

**Table 6:** Summary of weld metal, impact properties and sigma (σ) % in the PWHT solution treated and WQ condition. The results of this table are shown graphically in figure 14 and plotted against the Norsok min average specification of 45J.

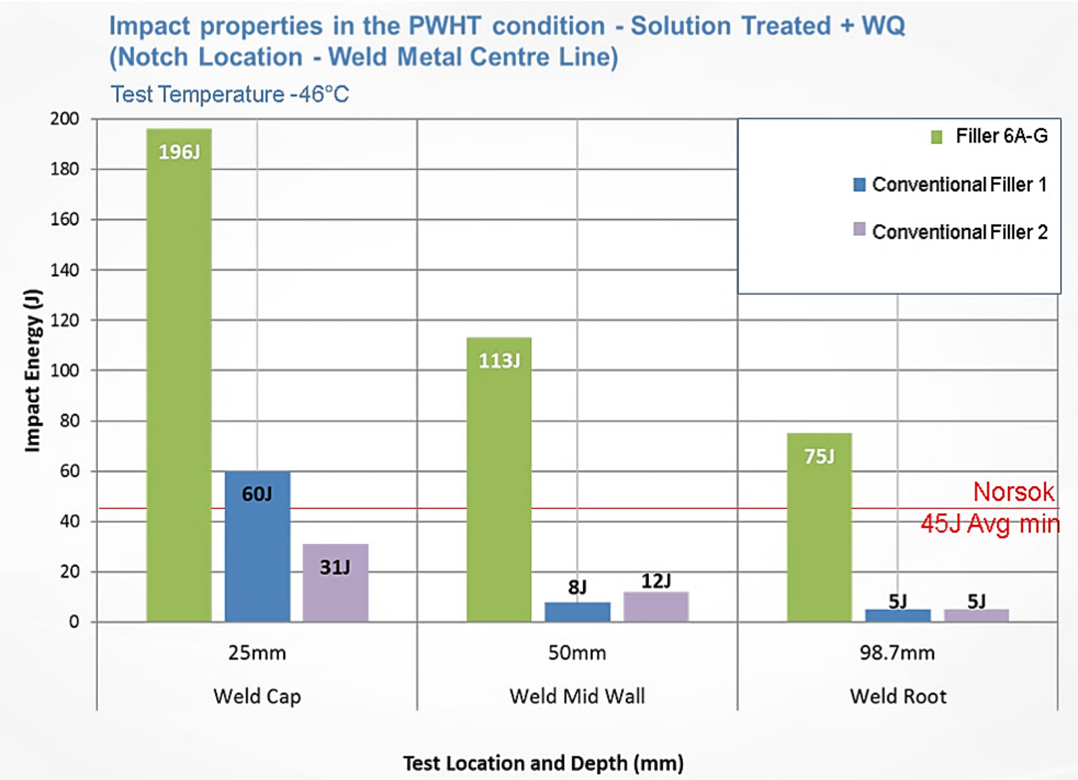


**Figure 14:** Impact property comparison of filler metals tested

Table 6, Fig 14, 15 and 16 shows one of the major findings of this work, which is that conventional fillers have a significant drop off in impact properties when welded in thick sections and subsequently post weld heat treated as mandated by ASTM A995 for duplex castings with welds of greater depth than 25mm and as a supplementary requirement for the same depth of weld repair for duplex castings to ASTM A890.

Table 6 details the effect of sigma (σ) precipitation in the weld metal at deferent depths. Conventional filler (1) show good impact strength at 25mm depth, while at 50mm depth impact values drop off rapidly to values lower than the Norsok industry minimum of 45J.

Standard weld qualification testing for repair welding, of castings to ASTM A488, ASME IX or oil and gas industry customer specifications do no give exact locations for impact specimen extraction. At best the impact locations in the weld are stipulated as mid wall and root, but don't detail the minimum section size of the test piece to simulate the same quench characteristics as the casting or their longitudinal location of extraction along the test piece.

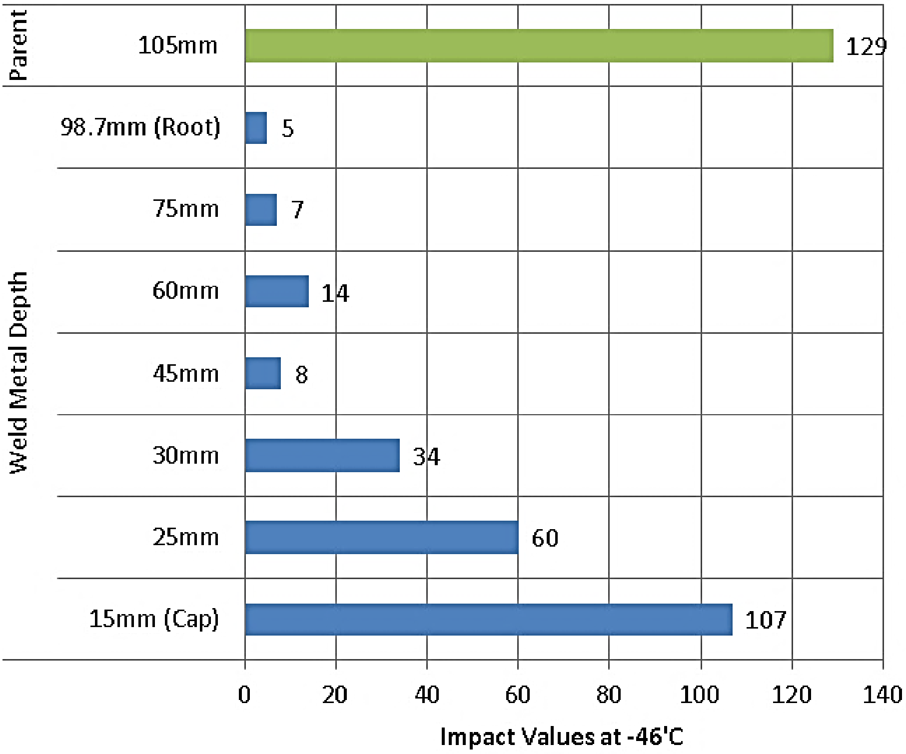


**Figure 15:** Conventional Filler (1) Reduction in average Impact as weld depth increases

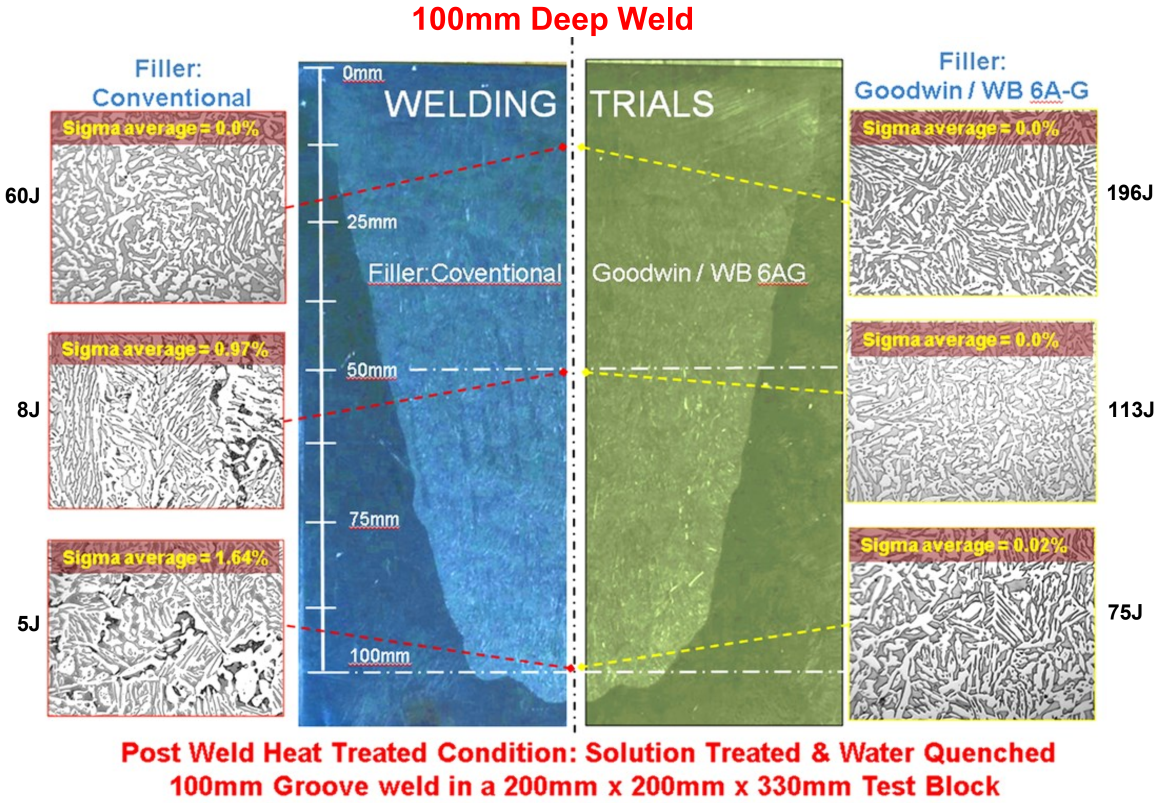
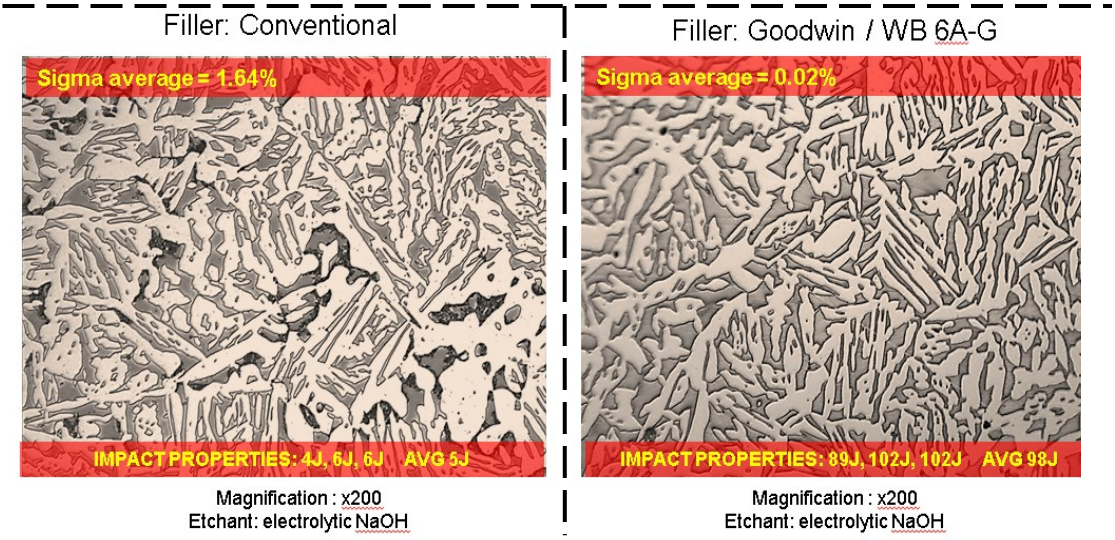


**Figure 16:** Deep Weld comparison of conventional filler (1) SDSS filler with 6A-G Filler Material – PWHT (Solution Treatment)

Fig.16 shows the comparison of intermetallic [sigma(σ)] precipitation in a 100mm deep weld, when one weld was performed using conventional filler as generic composition (1) as detailed in table 4, and a second weld completed using the new 6A-G filler metal. The impact properties for the 6A-G average 98J compared with just 5J for the conventional fillers at this root depth.

**Figure: 17** – Showing impact properties at 100mm depth for both filler options (weld root)



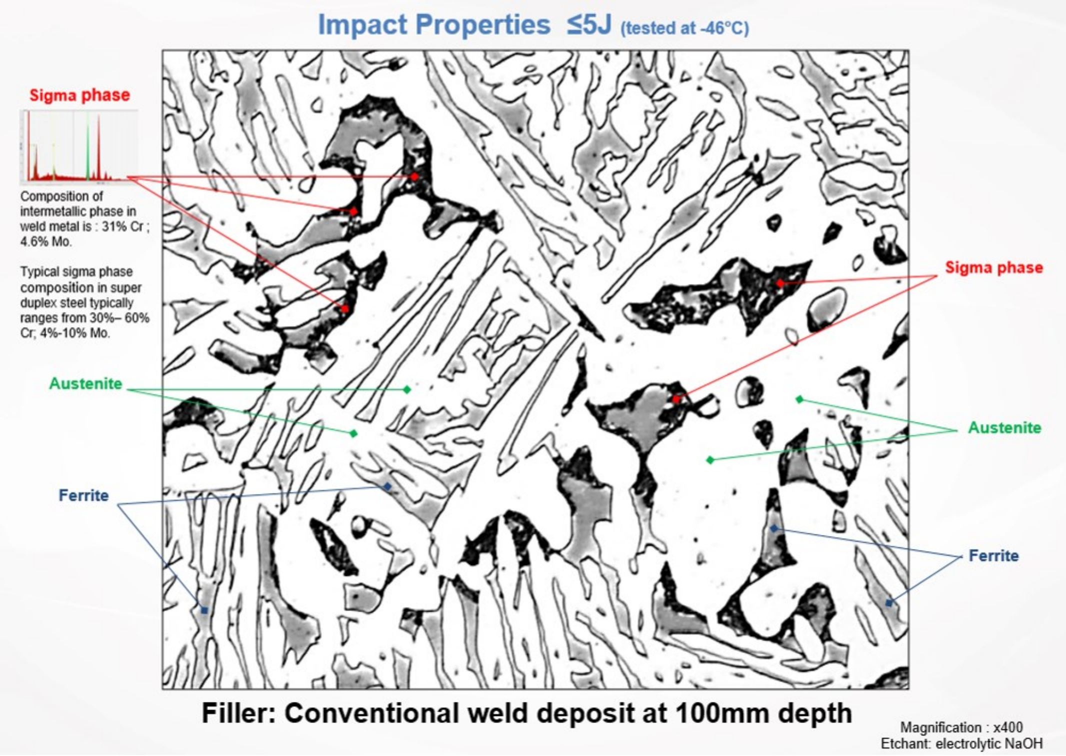
Filler: Conventional

Filler: Goodwin / WB 6A-G

Magnification : x200
Etchant: electrolytic NaOH

Magnification : x200
Etchant: electrolytic NaOH

**Figure 18:** Metallographic examination of conventional filler 100mm Deep Weld



Impact Properties ≤5J (tested at -46°C)

Composition of intermetallic phase in weld metal is : 31% Cr ; 4.6% Mo.

Typical sigma phase composition in super duplex steel typically ranges from 30%– 60% Cr; 4%-10% Mo.

Filler: Conventional weld deposit at 100mm depth

Magnification : x400
Etchant: electrolytic NaOH

At 100mm depth impact values are in single figures as a function of the precipitation of sigma phase. Conventional filler (2), which is close to parent matching chemistry, shows poor impact values in all section sizes. The low values of 31J at 25mm depth could not be explained which regards to sigma formations, but consistent with filler (1) as sigma precipitation commenced and increased with weld depth impact vales continued to reduce.

The new 6A-G filler metal only shows a comparative small reduction in impact properties as the weld depth increases, however even at the 100mm depth the impact properties at -46'C are over twice the minimum 45J required by most weld qualification requirements, and at 25mm depth the results are almost twice the value of the conventional filler. The 6A-G was also tested at all depths at -96'C with impact tests result values far in excess of the minimum 45J min requirement.

**Pitting Corrosion Test Results of 6A-G tested in both 'As Welded' and 'PWHT' conditions.**

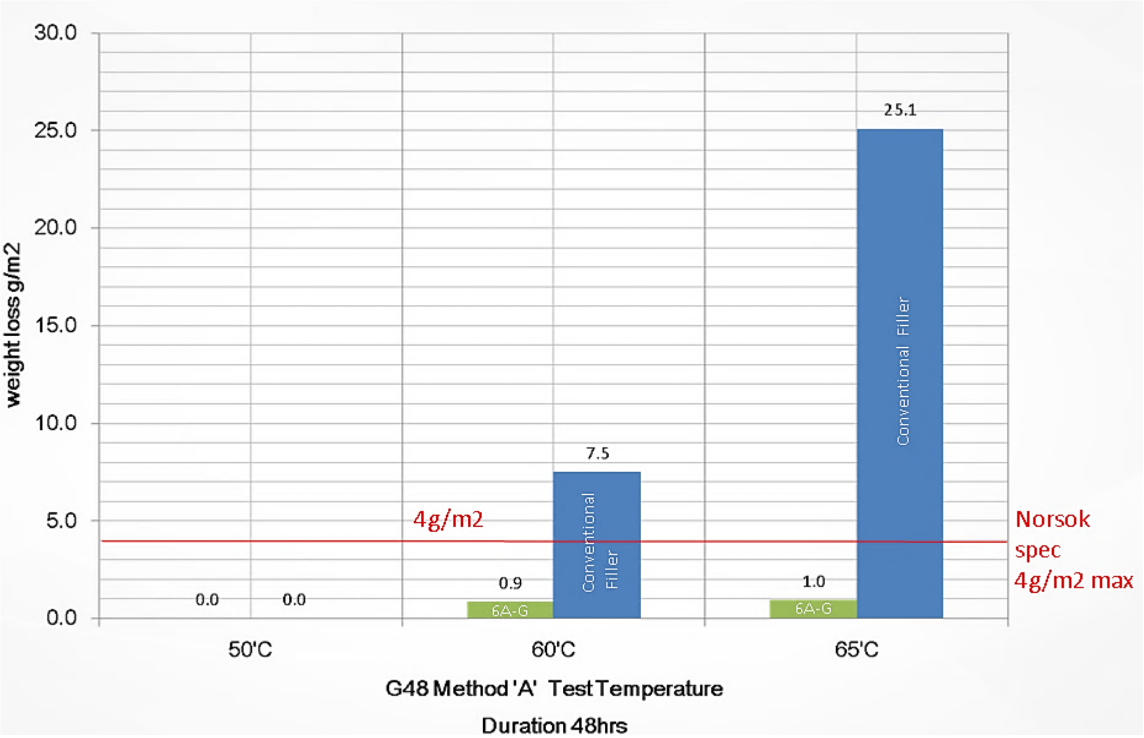


**Figure 19:** G48 Method 'A' - Pitting Corrosion property comparison of filler metals tested

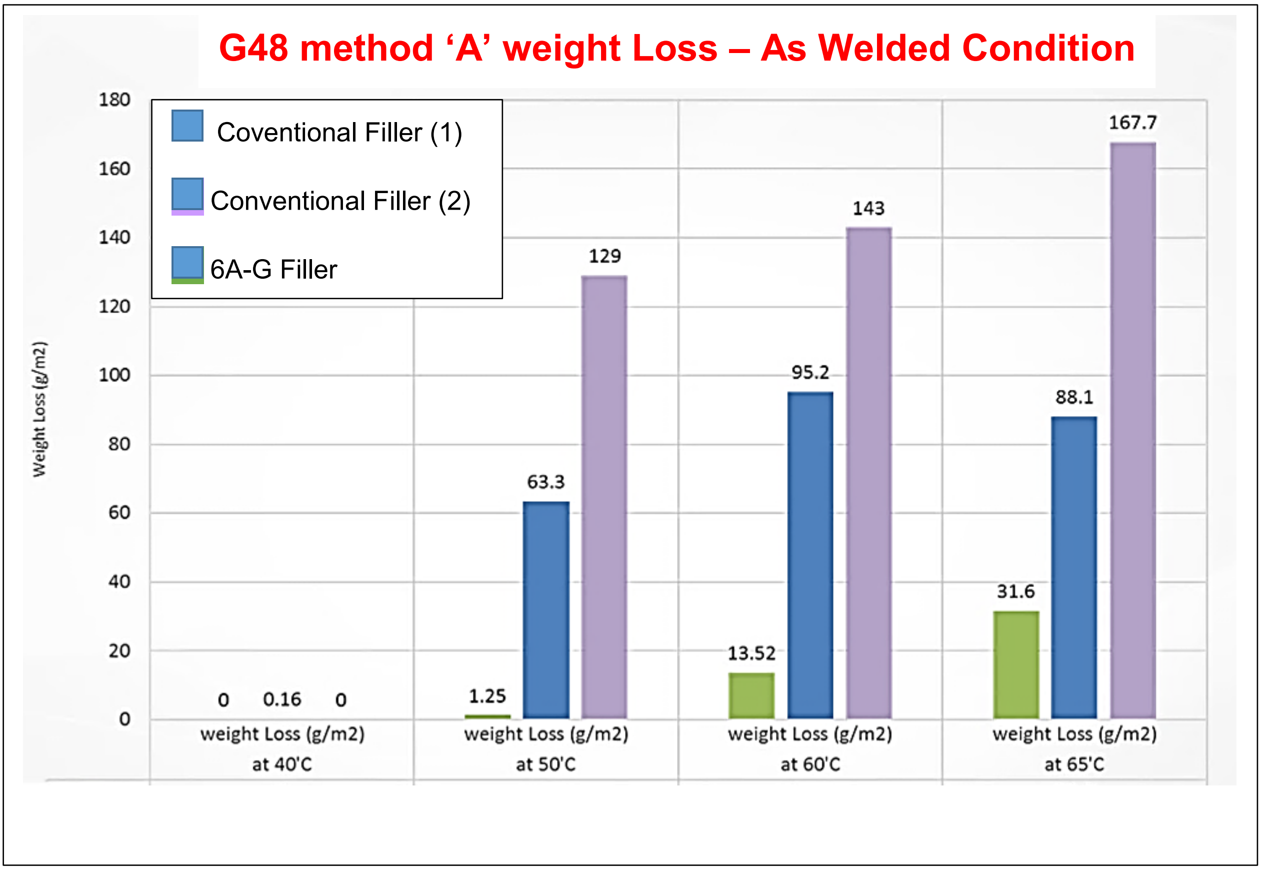


**Figure 20:** Comparison of filler metal properties in the as welded condition

G48 method A is specified in the oil industry to validate weld qualification procedural qualifications. In the 'as welded' the test temperature is specified at 40°C for a duration of 24hrs with a final maximum weight loss of 4g/$m^2$ with no visible pitting allowed. The acceptance criteria is specified for the PWHT weld, but with a higher test temperature of 50°C.

The new 6A-G weld material not only passed both criteria but surpassed each test condition by 10°C. (See fig 18 & 19).

## Conclusions:

1. The performance of the new cast, and weld metal material substantially surpasses what has historically been possible to consistently achieve in terms of low temperature impact and corrosion properties both in the post weld heat treated and as welded condition.

2. The low temperature performance of this new duplex steel also increases the envelope of operational conditions. The new 6A-G super duplex material can be confidently operated at temperatures down to -101ºC.

3. Welds made with 6A-G fillers can be succesfully made in heavy section components with tested weld depths down to 100mm, where previous limitations were between 25mm to 35mm before impact properties reduced to below the industry standard

4. The pitting corrosion properties have been dramically improved with the 6A-G material when tested using standard ferric chloride tests such as ASTM G48 method A and ASTM A923 method C. These tests are most often used screening tests for product in oil industry specifications to detect the presence of intermetallic phases and is the reason why these tests are performed at 1/4T and 1/2T locations where the media will never contact.

## Acyrnms and Abreveations:

**6A-G –** Goodwin modified SSDS 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 treated.

**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.

**(J)** – Joules (unit of anborbed energy during impact testing)

**(N/mm$^2$) –** unit of Force used in tesnile testing as a function of cross sectional area (Newtons per millimeter squared)

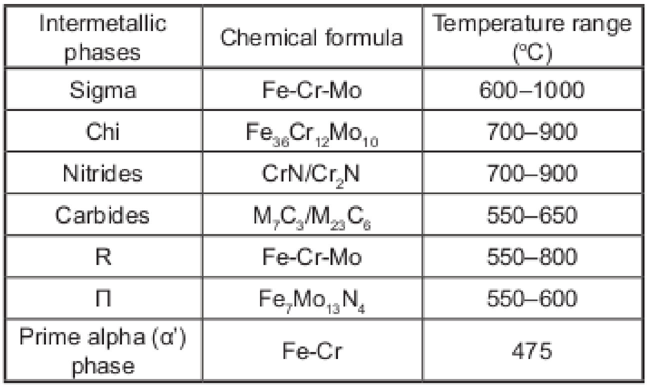
**(g/m$^2$)** – unit of weight loss used in corrosion testing as an caaeptance criteria (grammes per meter squared)

**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) -** NORSOK standards are developed by the Norwegian petroleum industry to ensure adequate safety, value adding and cost effectiveness for petroleum industry developments and operations. Furthermore, NORSOK standards are as far as possible intended to replace oil company specifications and serve as references in the authorities regulations.

### **Posible second phase precipitation in SDSS**[6]



| Intermetallic phases | Chemical formula | Temperature range (°C) |
|---|---|---|
| Sigma | Fe-Cr-Mo | 600–1000 |
| Chi | $Fe_{36}Cr_{12}Mo_{10}$ | 700–900 |
| Nitrides | $CrN/Cr_2N$ | 700–900 |
| Carbides | $M_7C_3/M_{23}C_6$ | 550–650 |
| R | Fe-Cr-Mo | 550–800 |
| Π | $Fe_7Mo_{13}N_4$ | 550–600 |
| Prime alpha (α') phase | Fe-Cr | 475 |

### **Key Phases Discussed in this Paper:**

**Sigma Phase** (σ) **–** This phase occurs due the eutectoid reaction where ferrite is converted to sigma and secondary austenite ($\gamma_2$).

$$\alpha \rightarrow \gamma_2 + \sigma$$ [1]

Sigma has the chemical formula Fe-Cr-Mo and precipitation temperature range is 600°C to 1000°C.

## Eqiupment:

a) Impacts testing perfromed to ASTM E8 and ASTM A370 using Avery Dension Impact machine 8mm striker. Charpy v notch Specimen size 10mm x10mm x 55mm.

b) Metallography performed using Olympus optical microscope and xyz visual software.

c) Scanning Electron assesments using Hitachi XYZ desktop SEM with EDS capability.

d) Intermetallic phase determination using EDS analysis of phase and % phase counting using XYZ software.

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