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(54) **Title**: A STEEL, A WELDING CONSUMABLE, A CAST, FORGED OR WROUGHT PRODUCT, A METHOD OF WELDING, A WELDED PRODUCT AND A METHOD OF HEAT TREATING

Fig. 2

Example No	C	Si	Mn	S	P	Ni	Cr	Cu	Mo	Nb	W	V	Al	N2	Co	200mm 1/2T	Av.	150mm 1/2T	Av.
1*	0.016*	0.32	0.82	0.005	0.026	7.92	24.48	0.74	3.51	0.002	0.71	0.048	0.007	0.24	0.07	108,120,110	113		
2	0.013	0.22	0.74	0.001	0.027	7.80	24.95	0.66	3.60	0.001	0.70	0.06	0.009	0.22	0.048	133,130,153	139		
3	0.015	0.31	0.90	0.004	0.026	7.92	24.93	0.75	3.70	0.001	0.63	0.046	0.010	0.22	0.06			135,149,151	145
4	0.015	0.27	0.85	0.004	0.027	8.02	24.92	0.72	3.59	<0.001	0.68	0.051	0.008	0.245	0.066	156,108,106	124		
5	0.014	0.33	0.88	0.006	0.03	7.46	25.01	0.76	3.56	0.006	0.68	0.054	0.009	0.23	0.1	109,112,141	121		
6*	0.017*	0.33	0.88	0.005	0.029	7.09*	25.44	0.76	3.5	0.004	0.68	0.056	0.008	0.28	0.21	79,74,73	75		
7*	0.017*	0.54*	0.82	0.006	0.024	8.05	24.66	0.74	3.66	0.003	0.66	0.058	0.008	0.21	0.69	92,65,62	73		
8*	0.017*	0.6*	0.88	0.005	0.027	7.26*	25.43	0.66	3.02	0.025*	0.57	0.06	0.024	0.27	0.091	63,54,70	62		
9*	0.022*	0.43*	0.73	0.007	0.028	7.41*	25.05	0.73	3.64	0.014	0.67	0.055	0.009	0.25	0.09	63,53,66	61		
10*	0.0146	0.35*	0.83	0.005	0.026	7.27*	25.26	0.076	3.59	0.013*	0.68	0.064	0.009	0.28	0.07	86,64,66	72		
11*	0.013	0.4*	0.8	0.007	0.027	7.42*	25.08	0.73	3.58	0.014	0.67	0.06	0.009	0.27	0.08	75,54,80	70		
12+	0.015	0.32	0.85	0.003	0.025	7.98	24.93	0.69	3.64	0.006	0.68	0.05	0.010	0.25	0.06	91,71,98	87		

(* outside scope of invention)
(+ inside scope of invention but different heat treatment to other examples applied)

(57) **Abstract**: A steel including, in mass %: 0.005 to 0.015% carbon; 0.05 to 0.35% silicon, 7.45 to 8.4% nickel; 1.00%> or less manganese; 0.025%> or less sulphur; 0.030%> or less phosphorous; 24.0 to 26.0% chromium; 0.50 to 1.00% copper; 3.0 to 4.0% molybdenum; 0.002 to 0.010% niobium; 0.75% or less cobalt; 0.015% or less aluminium; 0.20 to 0.30% nitrogen; 0.50 to 0.85%) tungsten; the balance being iron and incidental impurities.

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A Steel, a Welding Consumable, a Cast, Forged or Wrought Product, a Method of Welding, a Welded Product and a Method of Heat Treating

The present invention relates to a steel, a welding consumable, a cast, forged or wrought product, a method of welding, a welded product and a method of heat treating. In particular the invention relates to steels such as those falling under the designation ASTM A995-13 Gr 6A, 1 December 2013 and to a welding consumable suitable for welding such steels and similar steels as well as a heat treatment suitable for such steels whether welded or not.

ASTM A995-13 Gr 6A, 1 December 2013 (6A) is a 25 % Chrome Super Duplex stainless steel (comprising mainly ferrite and austenite). Such Super Duplex steels have been made for over 40 years. Super Duplex stainless steels are extensively used where higher strength and corrosion resistance is required as compared to conventional 18/8/3 stainless steels such as 316 or the cast version ASTM A351 CF8M.

Traditionally CF8M has been and still is used for cryogenic applications such as liquefied natural gas (LNG) facilities. This is because CF8M provides good impact properties down to -196 Degrees C even in thick wall sections whereas Super Duplex stainless steel such as ASTM A995-13 6A, 1 December 2013 traditionally only has reasonable impact properties down to -46 degrees C and even then not at ½ thickness (T1/2) in very thick wall components where the wall thickness is 200mm or even 250mm and larger.

It is for this reason that the Norsok specification M630 for grade 6A only requires impact testing to be carried out at -46 Degrees C and for the following condition to be met for production castings.

Norsok M630 material data sheet MDS-D56: 45J average / 35J single minimum at -46° ¼ thickness (T1/4)

Norsok write many material specifications having researched globally what is best practice and what is achievable from high quality manufacturers. The Norsok specifications are used by many metallurgists and engineering designers, especially in the oil and gas industry, as an authoritative guide as to what metallurgical properties are possible to achieve in different alloys.

Many 25 % Cr Super Duplex stainless steel castings have been made for over 40 years. However, it has not been possible to guarantee higher impact properties at -46 degrees C than that which is specified in the Norsok Specification and even then not in thick walled components (e.g. with a thickness of over 150 mm or over 200mm or over 250mm).

The present invention relates to a specific chemistry for a ASTM A995-13 Gr 6A, 1 December 2013 type Super Duplex alloy that consistently provides superior impact properties up to 150 % higher than the Norsok specification at – 46 Degrees C and also provides acceptable impact properties (45J Av / 35J Min) at - 101 Degrees C.

The ASTM A488 weld qualification standard does not call up deep impact testing (that is through the depth of the weld) and nearly all impact testing of weld metal is normally carried out near the weld cap rather than the weld root.

It is for this reason that there is little knowledge of impact properties in thick Duplex welds. Data generated by an extensive programme of testing using commercially available Duplex welding wire or electrodes have shown that the impact properties of Weld metal at -46 Deg C in post weld solution treated castings severely decrease the further the tests progress down from the weld cap . At between 50mm and 100mm deep the impact properties are unacceptable as they are often in the single figures.

The adoption of the same or similar chemistry restrictions as determined in the inventive steel when applied to welding electrodes for 25% Cr Super Duplex alloy also provides greatly enhanced impact properties in weld metal deeper down from the weld cap than 25mm.

The present invention provides a steel including or consisting of, in mass %: 0.005 to 0.015% carbon; 0.05 to 0.35% silicon, 7.45 to 8.4% nickel; 1.00% or less manganese; 0.025% or less sulphur; 0.030% or less phosphorous; 24.0 to 26.0% chromium; 0.50 to 1.00% copper; 3.0 to 4.0% molybdenum; 0.75% or less cobalt; 0.010% or less niobium;0.015% or less aluminium; 0.20 to 0.30% nitrogen and 0.50 to 0.85% tungsten; the balance being iron and incidental impurities.

The adoption of the specific chemistry of the present invention controls on C, Si, Ni, Nb, and W (to minimise the presence of sigma phase) of the present invention result in the following:

1) Impact properties in ASTM A995-13 6A, 1 December 2013 that achieve up to and beyond 140J average / 100J single minimum at -46°C at both ¼ and ½ T in 200mm thick sections and that still achieve the required Yield, UTS, elongation and corrosion properties as specified in the ASTM specification

2) Impact properties at -101 Deg C in ASTM A995-13 6A, 1 December 2013 in 200mm thick sections that consistently achieve 45J Av and 35 J Minimum.

This level of mechanical performance and safety margin has historically never been achievable with thick section castings on a consistent basis.

3) If the same or similar chemistry limitations that are tighter than the ASTM specification is applied to a welding consumable (e.g. filler weld metal and welding electrodes) then impact properties in 100mm deep weld in 200mm thick Super Duplex stainless steel such as ASTM A995 6A will, in the post weld heat treated (solution treated and water quenched) or in the as-welded condition provide impact properties of up to 100J average / 80J single at -46°C throughout the weld section thickness.

The present invention therefore provides a welding consumable including or consisting of, in mass %: 0.015 % or less carbon; 0.05 to 0.35% silicon, 7.45 to 10.5% nickel; 2.00% or less manganese; 0.025% or less sulphur; 0.030% or less phosphorous; 24.0 to 27.0% chromium; 0.00 to 1.00% copper; 3.0 to 4.5% molybdenum; 0.75% or less cobalt; 0.010% or less niobium; 0.015% or less aluminium; 0.20 to 0.30% nitrogen; 0.00 to 1.00% tungsten; the balance being iron and incidental impurities.

The present invention further provides for the use of the steel or welding consumable in a liquid petroleum gas (LPG) facility.

The present invention further provides a preferred method of heat treating a cast or forged or wrought product of a duplex stainless steel in the welded or unwelded condition, comprising: raising the temperature of the product to a first temperature between 1100 and 1150 deg C and holding at the first temperature; lowering the temperature of the product to a second temperature between 1040 and 1070 deg C and holding at the second temperature; and quenching the product in water from the second temperature. The casting or forging may be heat treated more conventionally just by raising the temperature of the casting to a first temperature between 1100 and 1150 deg C and holding at the first temperature. Both these two cycles also apply to welded castings.

The heat treatment associated with the present invention may be applied to the inventive steel and inventive welding consumable as well as other Super Duplex stainless steels. Control differs from the ASTM heat treatment in that it is 1120 Deg C holding to allow the casting to heat through (for about 1 hour per inch of maximum casting cross section) followed by dropping the temperature to 1050 Deg C and holding for a further time (e.g. 5 hours) followed by a water quench.

The adoption of this heat treatment process, or in the case of welding no post weld heat treatment at all, will still produce impact properties some 50 % better than normal with the enhanced chemistry, but the stepped heat treatment of the present invention further improves the impact properties of both the base metal/steel of the present invention and the weld made of the welding consumable of the present invention.

The duplex stainless steel of the present invention has high impact properties in castings in the heat treated state. An already heat treated casting may be welded with a filler or rod to the invention chemistry and not subjected to post weld heat treatment and still have excellent impact resistance in both the base cast metal and the weld metal. The superior impact resistance and corrosion resistance is thought to be the result of a lower volume fraction of sigma phase in the microstructure of the steel. Sigma phase is an intermetallic compound which can be present in duplex stainless steel in addition to the austenite and ferrite which make up the remainder of the microstructure along with carbides, nitrides etc.. The absence of substantial amounts of sigma phase also means that large castings do not crack on having their temperature raised and lowered during heat treatment. Previously even raising the temperature slowly of a Super Duplex large casting has resulted in cracking of the casting.

The present invention will now be described by way of non-limiting example with reference to the following drawings.

Figure 1 is a table of the range of composition for a ASTM A995-13 Gr 6A dated 1 December 2013 steel

Figure 2 is a table of compositions and impact strengths of examples of the invention and comparative examples;

Figure 3 is a table of compositions and impact strengths of examples of the invention;

Figure 4 is a table of a welding consumable composition example;

Figure 5 is a schematic illustration of the dimensions of a 200mm weld test plate;

Figure 6 is a table showing impact results for a weld made of the welding consumable in Figure 4;

Figure 7 is a bar graph showing the improvement in impact resistance of a welding consumable of the presention invention compared to conventional weld consumable in the as welded condition; and

Figure 8 is a bar graph showing the improvement in impact resistance of a welding consumable of the presention invention compared to conventional weld consumable in the post weld heat treated condition.

The present invention relates to a steel with a composition which falls within ASTM A995-13 Gr 6A, 1 December 2013 and which has a tighter composition to increase low temperature impact resistance particularly in thick sections and at high depths, whilst maintaining the other physical requirements of ASTM A995-13 Gr 6A, 1 December 2013 such as yield, UTS, elongation, and corrosion resistance. It is thought that the inventive steel also has improved corrosion resistance compared to other steels falling in ASTM A995-13 Gr 6A, 1 December 2013. Improved corrosion resistance is also achieved.

In the present invention, compared to ASTM A995-13 duplex Grade 6A, 1 December 2013 the silicon content is relatively limited and/or the nickel content is relatively raised as well as specific quantities of carbon and tungsten, combined with limiting the amounts of niobium and aluminium result in the improved properties, thought to be at least in part due to the reduction in the presence of sigma phase that is formed during quenching following the solution heat treatment at the nominal 1120 Deg C

The reasons for restricting the chemical composition of the duplex stainless steel of the present invention compared to ASTM A995-13 Gr 6A, 1 December 2013 will now be described. An explanation of the effect of additions which are not varied from the ASTM standard is omitted.

All percentages are weight percent unless otherwise indicated. The term “consisting of” is used herein to indicate that 100% of the composition is being referred to and the presence of additional components is excluded so that the percentages add up to 100%.

Carbon (C)

Carbon is effective for stabilizing austenitic phases. A preferred amount is 0.005% or more. However, the amount of carbon is limited as its solubility in both ferrite and austenite is limited. Thereby limiting the carbon amount to 0.020%, namely 0.005 to 0.020, reduces the risk of precipitation of carbides, particularly chromium carbides. Experiments have shown that limiting the carbon even further results in even higher impact resistance. In the invention, carbon is limited to 0.015% or less, preferably 0.0145% or less. Particularly for welding consumables (e.g. electrodes) a lower level of carbon of 0.0145% or less is preferred.

Silicon (Si)

Silicon is present as a deoxidizer. A minimum amount of silicon of 0.05% or more, preferably 0.1% or more achieves sufficient deoxidation. However, the presence of silicon can lead to precipitation of unwanted intermetallic phases, including sigma phase. Therefore, the amount of silicon is limited to 0.35 mass per cent but preferably to 0.30% and preferably to 0.25%. It has been found that for higher levels of silicon, its presence in castings can be mitigated to some extent by high nickel composition as shown by the examples described below. Preferably the amount of silicon is limited to 0.30% or even 0.25% thereby to reduce the chance of sigma phase precipitation. The best properties are achieved with a combination of low silicon content (0.35% or less or preferably 0.30% or less and preferably 0.25% or less) combined with high nickel content of 7.45 to 8.4% or preferably 7.5 to 8.4%, more preferably 7.8 to 8.4% and more preferably 8.05 to 8.4% and most preferably 8.1 to 8.4%. Nickel content of 7.45 to below 7.8% achieves high impact performance, but impact performance improves even further at 7.8% or more nickel.

Nickel (Ni)

Nickel is an austenite stabilizing element. Experiments have shown that increased nickel content improves impact resistance. A minimum amount of nickel of 7.45% leads to high impact resistance in the case that the presence of silicon is limited to 0.35% or less. A minimum amount of 7.8 % nickel achieves high impact resistance even at relatively high levels of silicon of up to 0.45 %. However, best results are achieved, whatever the level of silicon, at levels of nickel of 7.45% to 8.4%, preferably 7.5% to 8.4% and more preferably 7.8 to 8.4% and even more preferably 8.05 to 8.4% and most preferably 8.10 to 8.4%.

Niobium (Nb)

Niobium is not referenced in the ASTM A995-13, 1 December 2013 standard. However, Niobium is detrimental to impact properties by the formation of carbides and/or nitrides as discovered by the present inventors. Niobium has an high affinity for nitrogen and as such more specifically forms nitrides that combine with the nitrogen present in the steel as an intentional alloying element. Niobium is preferably present in an amount of 0.002% or more or 0.003% or more. However, the presence of niobium in amounts of greater than 0.017% can lead to a reduction in the impact strength of the steel as shown by the attached examples. Therefore, the amount of niobium is limited to 0.010% for best performance. A level of 0.010% or less niobium is very low compared to most steels manufactured, which normally have a level of at least 0.015% up to 0.03%, though the precise level is often not controlled or reported because of niobium's prevalence at these concentrations. The ASTM specifications do not place any limitation on the level of niobium. In order to achieve a low niobium concentration, argon oxygen decarburization (AOD) refining or induction melting of pure chrome and also the use of ARMCO is necessary. In AOD refining temperature and silicon concentration are controlled whilst oxygen is blown in order to remove niobium whilst not removing other elements. The advantage of using the AOD process is that scrap metal (e.g. stainless, plate etc) can be used to keep the cost of raw materials down. For induction melting scrap metal may not be used as scrap contains too much niobium and so expensive starting materials need to be purchased.

Tungsten (W)

Tungsten improves corrosion resistance, particularly resistance to pitting and crevice corrosion. In the present invention the amount of tungsten is between 0.50 to 0.85% as experiments have shown that this provides the best range for good impact resistance at low temperatures. Preferably the amount of tungsten is 0.64 to 0.84% or 0.66 to 0.84%.

Aluminium

Aluminium is not referenced in the ASTM A995-13, 1 December 2013 standard. However, the amount of aluminium should be limited in order to reduce the precipitation of aluminium nitride, the presence of which can result in a loss of corrosion resistance and toughness. Therefore, the amount of aluminium is limited to 0.015% or less, preferably 0.010% or less.

Sulphur

A lower level of sulphur than allowed by the ASTM specification is preferred to avoid the formation of sulphides in the steel and so improve impact resistance. A level of sulphur of 0.010% or less is preferred.

Cobalt

Cobalt is often present in source nickel as the two elements are found together. Cobalt behaves in a similar way to nickel and so can be present at 0.75% or less, preferably 0.60% or less, more preferably 0.50% or less and most preferably 0.20% or less.

Incidental impurities may be present, preferably up to a maximum of 0.20%. Vanadium can be seen as an incidental impurity. Preferably vanadium is present at a level of 0.10% or less.

The presence of sigma phase can deleteriously effect impact resistance. Therefore preferably the volume fraction sigma phase in the steel is less than 0.25%, preferably less than 0.1%, most preferably no detectable sigma phase as measured under any of the procedures in ASTM A923 2014, preferably ASTM A923-14 method C.

Preferred Steel

A preferred steel includes or consists of, in mass %: 0.005 to 0.015% carbon; 0.05 to 0.35 (or preferably 0.30%) silicon, 7.45 to 8.4% nickel (preferably 7.8 to 8.4% nickel); 1.00% or less manganese; 0.025% or less sulphur; 0.030% or less phosphorous; 24.0 to 26.0% chromium; 0.50 to 1.00% copper; 3.0 to 4.0% molybdenum; 0.75% or less cobalt; 0.010% or less niobium;0.015% or less aluminium; 0.20 to 0.30% nitrogen and 0.50 to 0.85% tungsten; the balance being iron and incidental impurities. Even more preferably the preferred steel includes or comprises 0.25% or less silicon and/or 0.0145% or less carbon and/or 8.0% or more nickel and/or 8.05% or more nickel and/or 0.010% or less sulphur and/or 0.002% or more niobium and/or 0.003% or more niobium.

Preferred welding consumable

A preferred welding consumable includes or consists of, in mass %: 0.015% or less carbon; 0.05 to 0.35 (or preferably 0.30%) silicon, 7.45 to 10.5% nickel (preferably 7.8 to 10.5% nickel); 2.00% or less manganese; 0.025% or less sulphur; 0.030% or less phosphorous; 24.0 to 27.0% chromium; 0.00 to 1.00% copper; 3.0 to 4.5% molybdenum; 0.75% or less cobalt; 0.010% or less niobium;0.015% or less aluminium; 0.20 to 0.30% nitrogen and 0.00 to 1.00% tungsten; the balance being iron and incidental impurities. Even more preferably the preferred welding consumable includes or comprises 0.25% or less silicon and/or 0.0145% or less carbon and/or 8.0% or more nickel and/or 8.05% or more nickel and/or 9.1% or more nickel and/or 9.3% or more nickel and/or 9.4% or more nickel and/or 0.010% or less sulphur and/or 0.002% or more niobium and/or 0.003% or more niobium.

Example

Super Duplex stainless steels having the chemical composition shown in Figure 2 were prepared. Castings of 200 mm thickness were prepared. These castings were heat treated at 1120°C where they were held for a time to allow through heating (e.g. 1 hour for every inch of thickness) before the temperature was dropped to 1050°C and held for five hours, followed by a water quench. In the case of example 3 the casting was 150 mm thick.

The heat treatment is designed such that all sigma phase dissolves in the austenite and ferrite phases at 1120°C. The temperature is then dropped to 1050°C, just above the solvus temperature of sigma, such that the maximum cooling rate can be achieved through out the thickness of the casting so as to avoid sigma and nitride precipitation as much as possible during cooling.

Charpy Impact tests were carried out using 10mm x 10mm x 55mm specimens to ASTM E23 Standard "Test methods for Notched Bar Impact Testing of Metallic Materials" revision 2012-C, at -46°C at half thickness and the results are given in figure 2.

As can be seen from figure 2, all of the examples in Table 1 have a composition falling within ASTM A995 Gr 6A, 1 December 2013. However, only those examples which are limited in carbon concentration to below 0.02%, in silicon concentration to 0.05-

0.35% where the nickel concentration is between 7.10 and 8.4% or in silicon concentration to 0.05-0.45 % and a nickel concentration of 7.8 to 8.4%, have a niobium content of 0.017% or less, an aluminium content of 0.015% or less and a tungsten composition of 0. 50-0.85% achieve an average impact strength of above 120 Joules and a minimum of three tests of above 108 Joules. Vanadium is present as an incidental impurity. Cobalt is present less than 0.75%. Cobalt is present because is often present with nickel sources.

In the present invention an average impact strength (for a 200mm thick product) at ½ T is preferably at least 100 J and a minimum of three tests 80 J or more as measured by ASTM E23, 2012-C at -46°C.

Examples 2-4 are best performing in terms of impact strength and they have a silicon concentration of 0.05-0.35% as well as a nickel concentration of 7.8-8.4%. Examples 2 and 4 have best performance and fall within the most preferred composition with levels of carbon at or below 0.015% and silicon below 0.30% and at least 7.8% Ni. Example 5 has low carbon and silicon concentrations of 0.014% and 0.33% respectively and a reasonably high nickel concentration of 7.46%. This combination results in an impact strength of 121 Joules which is better than example 1, which has a higher carbon concentration.

Examples 6-11 fall compositionally outside the scope of the present invention and have impact resistances lower than 80 Joules. However even these examples exhibit increased impact resistance compared to the impact resistance achieved with 6A steels until now.

Example 6 has a low silicon concentration of 0.33%, but due to its low nickel concentration of 7.09% only has an impact strength of 75 Joules.

All of examples 8-11 include silicon and nickel in amounts falling outside the scope of the present invention and resulting in low impact strengths between 62 and 72 Joules.

Example 12 has a relatively low impact strength compared to examples 1-5 of 90 Joules. However example 12 was heat treated in a single step with a solution heat treatment at 1120 deg C for 10 hours followed by a water quench. This is thought to be the reason for the lower impact resistance compared with examples 1-5, though the impact resistance is better than that of examples 6-11 which fall outside the preferred composition but did have the two step heat treatment of the invention applied. The best performing examples of Figure 2 (examples 2-5 and 12) all have 0.015% or less carbon, 0.35% or less silicon, 0.010% or less niobium and 7.45% or more nickel.

Example 12 shows the improvement in impact resistance achieved by applying the two step heat treatment of the present invention and also shows that the steel composition of the present invention achieves benefits in impact resistance even with a conventional heat treatment.

Thus the method of heat treating of the present invention is a two stage heat treatment comprising raising the temperature of the casting to a first temperature where the sigma phase dissolves in the austenite and ferrite phases. The first temperature is in the range of 1100 to 1150 deg C. The casting is held at the first temperature for long enough for the casting to heat through such that the whole of the casting reaches the first temperature. As an example, the casting may be held at the first temperature for a minimum time in hours of the (maximum) thickness of the casting in inches divided by 2, preferably by 1 (i.e. one hour for each inch of thickness). The temperature of the casting is then reduced to a second temperature just above the solvus point of the sigma phase. The second temperature may be in the range of 1040 to 1070 deg C so long as it is above the sigma solvus temperature. The casting is held there long enough for the temperature to stabilize. As an example, the casting may be held at the second temperature for a minimum time in hours of the (maximum) thickness of the casting in inches divided by 4, preferably by 2 (i.e. half an hour for each inch of thickness). For example the casting is held there for 3 hours or more, for example for 5 hours. The time spent at each of the first and second temperatures is preferably limited to avoid excessive grain growth. The time spent at the first and second temperatures preferably does not exceed twice the maximum minimum amount of time specified above.

Figure 3 shows the results of further experiments which build on the results of Figure 2. Figure 3 includes results of corrosion tests, UTS and yield strengths as well as impact testing results for different casting sizes and at different temperatures. The way in which the castings were produced and tested are the same as explained with reference to examples 1-11 of Figure 2 except for the casting compositions, sizes and temperature of the impact tests which are detailed in Figure 3.

Example E has a composition close to that of example 4 and performs well in impact resistance at 50 and 100 mm 1/2T at all temperatures. Thus examples 2 and 4 and

A-E show that limiting silicon to 0.30%, carbon to 0.015% and having at least 7.8% nickel with niobium below 0.010% results in very good impact properties. However, examples A, B, C and D, with even further limited carbon and silicon concentrations, perform even better in this regard without a loss in performance in the other areas tested.

Examples A-D show it is possible to achieve an average impact strength at 1/2T of 140J or more and a minimum of these tests of 105J or more as measured by ASTM E23, 2012-C at -46°C for section sizes of at least 50 mm and upto 150 mm (and expected at 200 mm). At -76°C averages of at least 90J and a minimum of 65J or more is achievable and at -101°C an average of at least 60J and a minimum of 45J can be achieved.

The corrosion results at 60°C compare with a weight loss of 8-65 g/m^2 in 24 hours measured for conventional 6A chemistry falling outside the present invention as reported in " Forging ahead with improvements in impact properties and corrosion resistance" S. Roberts, ASTM A995 Gr 6A demands a weight loss of less than 4 g/m^2 at 50°C, which is easily achieved by the present invention.

Large castings of Super Duplex stainless steel often require welding. This is either to join components (or parts of components) together or perhaps more commonly as weld repairs of casting defects. As described elsewhere, the impact resistance of welds at large thicknesses has not previously been investigated because the relevant ASTM standard does not require testing of welds at large thicknesses. Tests have shown that deep welds in 6A duplex using welding rods currently available achieve very low impact resistance at high depths (e.g. 25mm, 50 mm, 75mm and 98.5 mm) for a 100mm deep weld in a 200mm section thick casting. Often such welds have only achieved an impact resistance at such depths at -46 deg C of a few tens of Joules, and not consistently through out the depth and/or width of the weld.

The present inventors have found that by adopting the composition of the steel of the present invention in welding consumables when welding 6A steels, the impact resistances at high depths and across the width of the weld are vastly improved. In fact, it appears that even better impact properties of the weld can be achieved at higher nickel concentrations and lower carbon concentrations. This ensures a balance ferrite in the as welded condition. So the present invention allows for the welding consumable to have a composition of the steel of the present invention except for nickel content of up to 10.5% (preferably of up to 10.0%) and limit carbon to 0.015% or less, preferably 0.0145% or less carbon. In an embodiment the welding consumable has 8.05% or more nickel, preferably 8.1% or more nickel, more preferably 9.1% or more nickel, still more preferably 9.3% or more nickel and most preferably 9.4% or more nickel. Increasing nickel concentrations are thought further to minimise sigma formation. In an embodiment compared to the base metal the amount of manganese may be increased to up to 2.00% as this can improve weldability. Reduced amounts of copper and tungsten are allowed in an embodiment compared to the base metal (0.00 to 1.00% and 0.00 to 1.00% respectively) to take into account 2507 type weld consumables which are not alloyed with either element. Compared to the base metal more chromium (24.0 to 27.0%) and/or more molybdenum (3.0 to 4.5%) are allowed in an embodiment to allow for composition balance adjustments in the weld metal spec.

Figure 4 shows the composition of an example welding consumable. The welding consumable was used to fill a 100mm deep groove in a 200mm test plate whose dimensions are shown in Figure 5. Figure 6 shows the results of impact tests carried out at various depths through the weld metal, both in the as-welded condition (top) and in the post weld heat treated condition (the same conditions as applied to the castings described above, namely 1120 deg C followed by 1050 deg C and then a water quench). As the results show, the welding consumable of the present invention results in very high impact resistances in the as-welded condition and more than acceptable, though slightly lower, impact resistances in the heat treated condition.

Figure 7 is a bar chart showing the as welded impact energy in J on the y axis at -46°C for a 100 mm deep weld which is 90 mm in width in a 200 mm x 330 mm elongate block at different depths (25 mm, 50 mm and 98.7 mm) at the weld centre for a weld consumable (filler) according to the present invention (best results), a conventional weld consumable over alloyed with nickel (middle results) and a conventional weld consumable with a composition falling within the ASTM specification (worst results). The compositions of the two conventional fillers are as follows:

	C	**Si**	**Mn**	**S**	**P**	**Ni**	**Cr**	**Cu**	**W**	**Mo**	**N**
Over Alloyed Ni Filler	0.03	0.69	1.07	0.005	0.017	9.6	24.6	0.10	0.03	3.5	0.22

6A Matching Filler (Cu)	0.025	0.61	1.01	0.015	0.019	7.8	24.6	0.65	0.71	3.6	0.27

Figure 8 is the same as Figure 7 except that the samples are in the post weld heat treated condition, namely solution treatment of 1120°C for 1 hour per inch thickness, followed by 1050°C until equalised, followed by a water quench. The results in Figures 7 and 8 show the improvement in impact resistance of the present invention over conventional weld consumables.

CLAIMS

1. A steel including, in mass %: 0.005 to 0.015% carbon; 0.05 to 0.35% silicon, 7.45 to 8.4% nickel; 1.00% or less manganese; 0.025% or less sulphur; 0.030% or less phosphorous; 24.0 to 26.0% chromium; 0.50 to 1.00% copper; 3.0 to 4.0% molybdenum; 0.010% or less niobium; 0.75% or less cobalt; 0.015% or less aluminium; 0.20 to 0.30% nitrogen; 0.50 to 0.85% tungsten; the balance being iron and incidental impurities.

2. The steel of claim 1, including 7.5% or more nickel, preferably 7.8% or more nickel, most preferably 8.00% or more nickel.

3. The steel of claim 1, including 8.05% or more nickel.

4. The steel of any of claims 1-3, including 8.1% or more nickel.

5. The steel of any of the preceding claims, including 0.005 to 0.0145% carbon.

6. The steel of any of the preceding claims, including 0.05 to 0.30% silicon, preferably 0.05 to 0.25% silicon, most preferably 0.10 to 0.25% silicon.

7. The steel of any one of claims 1-6, including 0.002% or more niobium.

8. The steel of any one of claims 1-7, including 0.003% or more niobium.

9. The steel of any of claims 1-8, including 0.010% or less sulphur.

10. The steel of any one of claims 1-9, including 0.64 to 0.84% tungsten, preferably 0.66% to 0.84% tungsten.

11. The steel of any one of claims 1-10, including 0.010% or less aluminium.

12. The steel of any of claims 1-11, wherein a volume fraction of sigma phase in the steel is less than 0.25%, preferably less than 0.1%, most preferably no detectable sigma phase as measured under ASTM A923 2014.

13. The steel of any of claims 1-12, wherein the steel is a steel in accordance with ASTM A995-13 Gr 6A, 1 December 2013.

14. The steel of any of claims 1-13, wherein an average impact strength at ½ T is 100 J or more and a minimum of three tests of 80 J or more as measured by ASTM E23, 2012-C at -46°C.

15. The steel of any of claims 1-14, wherein an average impact strength at ½ T is 140 J or more and a minimum of three tests of 105 J or more as measured by ASTM E23, 2012-C at -46°C.

16. A cast, forged or wrought product formed of a steel according to any of claims 1-15.

17. A welding consumable including, in mass %: 0.015% or less carbon; 0.05 to 0.35% silicon, 7.45 to 10.5% nickel; 2.00% or less manganese; 0.025% or less sulphur; 0.030% or less phosphorous; 24.0 to 27.0% chromium; 0.00 to 1.00% copper; 3.0 to 4.5% molybdenum; 0.75% or less cobalt; 0.010% or less niobium; 0.015% or less aluminium; 0.20 to 0.30% nitrogen; 0.00 to 1.00% tungsten; the balance being iron and incidental impurities.

18. The welding consumable of claim 17, including 1.00% or less manganese and/or 24.0 to 26.0% chromium.

19. The welding consumable of claim 17 or 18, including 10.0% nickel or less;.

20. The welding consumable of claim 17 or 18, including 0.50 to 1.00% copper.

21. The welding consumable of claim 17 or 18, including 3.0 to 4.0% molybdenum; and 0.50 to 0.85% tungsten.

22. The welding consumable of any of claims 17 to 21, including 7.8% or more nickel, preferably 8.05% or more nickel, more preferably 8.1% or more nickel, still more preferably 9.1% or more nickel, still more preferably 9.3% or more nickel and most preferably 9.4% or more nickel.

23. The welding consumable of any of claims 17-22, including 0.01 to 0.015% carbon, preferably 0.005 to 0.0145% carbon.

24. The welding consumable of any of claims 17-23, including 0.05 to 0.30% silicon, preferably 0.10 to 0.25% silicon.

25. The welding consumable of any of claims 17-24, including 0.002% or more niobium.

26. The welding consumable of any of claims 17-25, including 0.003% or more niobium.

27. The welding consumable of any of claims 17-26, including 0.010% or less sulphur.

28. The welding consumable of any of claims 17-27, including 0.64 to 0.84% tungsten, preferably 0.66% to 0.84% tungsten.

29. The welding consumable of any of claims 17-28, including 0.010% or less aluminium.

30. The welding consumable of any one of claims 17-29, wherein the welding consumable is a filler weld metal or a welding electrode.

31. A method of welding a base steel using the welding consumable of any one of claims 17-30.

32. The method of welding of claim 31, wherein the base steel is in accordance with ASTM A995-13 Gr 6A, 1 December 2013.

33. The method of welding of claim 31 or 32, wherein the base steel is a steel according to any of claims 1-15.

34. The method of welding of any of claims 31-33, wherein the method is a method of forming a product according to claim 16.

35. A welded product comprising a base metal and a weld metal wherein the base metal is a duplex steel and the weld metal includes, in mass %: 0.015 % or less carbon; 0.05 to 0.35% silicon, 7.45 to 10.5% nickel; 2.00% or less manganese; 0.025% or less sulphur; 0.030% or less phosphorous; 24.0 to 27.0% chromium; 0.00 to 1.00% copper; 3.0 to 4.5% molybdenum; 0.75% or less cobalt; 0.010% or less niobium; 0.015% or less aluminium; 0.20 to 0.30% nitrogen; 0.00 to 1.00% tungsten; the balance being iron and incidental impurities.

36. The welding product of claim 35, including 10.0% nickel or less; 1.00% or less manganese; 24.0 to 26.0% chromium; 0.50 to 1.00% copper; 3.0 to 4.0% molybdenum; and 0.50 to 0.85% tungsten.

37. The welded product of claim 35 or 36, wherein the duplex steel is in accordance with ASTM A995-13 type Gr 6A, 1 December 2013.

38. The welded product of claim 35, 36 or 37, wherein the duplex steel is a steel according to any of claims 1-15.

39. A method of heat treating a cast or forged or wrought of a duplex stainless steel in the welded or unwelded condition, comprising: raising the temperature of the product to a

first temperature between 1100 and 1150 deg C and holding at the first temperature; lowering the temperature of the product to a second temperature between 1040 and 1070 deg C and holding at the second temperature; and quenching the product in water from the second temperature.

40. The method of claim 39, wherein the product is held at the first temperature for a time in hours of greater than the thickness of the product measured in inches divided by 2.

41. The method of claim 39 or 40, wherein the product is held at second temperature for a time in hours of greater than the thickness of the product measured in inches divided by 4.

42. The method of claim 39, 40 or 41 wherein the duplex steel is in accordance with ASTM A995-13 Gr 6A, 1 December 2013.

43. The method of any of claims 39 to 42, wherein the duplex steel is a steel according to any of claims 1-15.

44. A steel, cast, forged or wrought product, welding consumable or welded product substantially as herein before described with reference to and/or as illustrated in the accompanying drawings.

45. A method of welding or a method of heat treating substantially as herein before described with reference to and/or as illustrated in the accompanying drawings.

Fig. 1

	C	Si	Mn	S	P	Ni	Cr	Cu	Mo	Nb	W	V	Al	N2	Co
Spec min	-	-	-	-	-	6.5	24.0	0.50	3.0	-	0.50	-	-	0.20	-
Spec max	0.03	1.00	1.00	0.010	0.030	8.5	26.0	1.00	4.0	-	1.00	-	-	0.30	-

Fig. 2

Example No	C	Si	Mn	S	P	Ni	Cr	Cu	Mo	Nb	W	V	Al	N2	Co	200mm 1/2T	Av.	150mm 1/2T	Av.
1*	0.016*	0.32	0.82	0.005	0.026	7.92	24.48	0.74	3.51	0.002	0.71	0.048	0.007	0.24	0.07	108,120,110	113		
2	0.013	0.22	0.74	0.001	0.027	7.80	24.95	0.66	3.60	0.001	0.70	0.06	0.009	0.22	0.048	133,130,153	139		
3	0.015	0.31	0.90	0.004	0.026	7.92	24.98	0.75	3.70	0.001	0.63	0.046	0.010	0.22	0.06			135,149,151	145
4	0.015	0.27	0.85	0.004	0.027	8.02	24.92	0.72	3.59	<0.001	0.68	0.051	0.008	0.245	0.066	158,108,106	124		
5	0.014	0.33	0.88	0.006	0.03	7.46	25.01	0.76	3.56	0.006	0.68	0.054	0.009	0.23	0.1	109,112,141	121		
6*	0.017*	0.33	0.88	0.005	0.029	7.09*	25.44	0.76	3.5	0.004	0.68	0.056	0.008	0.28	0.21	79,74,73	75		
7*	0.017*	0.54*	0.82	0.006	0.024	8.05	24.66	0.74	3.66	0.003	0.66	0.058	0.008	0.21	0.69	92,65,62	73		
8*	0.017*	0.6*	0.88	0.005	0.027	7.26*	25.48	0.66	3.02	0.025*	0.57	0.06	0.024	0.27	0.091	63,54,70	62		
9*	0.022*	0.43*	0.73	0.007	0.028	7.41*	25.05	0.73	3.64	0.014	0.67	0.055	0.009	0.25	0.09	63,53,66	61		
10*	0.0146	0.36*	0.83	0.005	0.026	7.27*	25.26	0.076	3.59	0.018*	0.68	0.064	0.009	0.28	0.07	86,64,66	72		
11*	0.013	0.4*	0.8	0.007	0.027	7.42*	25.08	0.73	3.58	0.014	0.67	0.06	0.009	0.27	0.08	75,54,80	70		
12+	0.015	0.32	0.85	0.003	0.025	7.98	24.93	0.69	3.64	0.006	0.68	0.05	0.010	0.25	0.06	91,71,98	87		

(* outside scope of invention)

(+ inside scope of invention but different heat treatment to other examples applied)

Fig. 3

															ASTM G48 Corrosion				UTS	Yield	EL	RA							
															weight loss g/m2 (max <4g/m2)				690min	450min	25min	-	Low Temperature Impact testing results Joules						
No	C	Si	Mn	S	P	Ni	Cr	Cu	Mo	Nb	W	V	Al	N	50°C	55°C	60°C	65°C	UTS	Yield	EL	RA	Block size	Location	Temp °C	I1	I2	I3	AVG
A	0.011	0.25	0.85	0.002	0.023	8.38	24.4	0.74	3.77	0	0.71	0.053	0.01	0.21	0.0		0.0	0.0	771	495	39	64	50mm (2")	1/2T	-46	191	181	185	186
																			764	541	33	64	100mm (4")	1/2T	-46	177	178	180	178
																							100mm (4")	1/4T	-46	185	184	184	184
B	0.014	0.13	0.78	0.006	0.021	8.35	25.1	0.68	3.89	0	0.7	0.049	0.009	0.21	0.0		0.0	1.0	757	456	40	63	50mm (2")	1/2T	-50	180	180	182	181
																							50mm (2")	1/2T	-76	100	144	118	121
																							50mm (2")	1/2T	-101	86	146	105	112
																							300mm (12")	SUB	-46	96	85	112	98
																			725	469	25	43	300mm (12")	1/2T	-46	51	41	56	49
																							300mm (12")	1/4T	-46	72	73	83	76
																							300mm (12")	1/2T	-76	24	30	28	27
																							300mm (12")	1/2T	-101	27	18	18	21
C	0.013	0.240	0.750	0.003	0.025	8.130	25.390	0.660	3.790	0.001	0.690	0.047	0.007	0.250	0.0		0.0	0.0	765	483	36	64	50mm (2")	1/2T	-50	180	172	175	176
																							50mm (2")	1/4T	-50	172	171	170	171
																							50mm (2")	1/2T	-76	138	139	133	137
																							50mm (2")	1/2T	-101	65	68	71	68

Fig. 3 (Cont.)

D	0.013	0.16	0.8	0.003	0.029	8.19	25.1	0.69	3.57	>0.001	0.73	0.054	0.008	0.23	0.0	0.0	0.0	0.0	742	472	36	50	50mm (2")	1/2T	-50	170	162	161	164
																							50mm (2")	1/2T	-50	187	176	180	181
																			762	493	37	64	50mm (2")	1/4T	-46	194	171	172	179
																							50mm (2")	1/2T	-101	130	96	139	122
																							50mm (2")	1/2T	-76	165	163	168	165
																			763	525	45	63	150mm (6")	1/2T	-46	196	134	183	171
																							150mm (6")	1/2T	-46	197	194	196	196
E	0.015	0.260	0.830	0.004	0.025	8.150	25.100	0.690	3.680	0.000	0.700	0.039	0.007	0.220	0.0		0.0	0.0	746	522	33	64	50mm (2")	1/2T	-50	158	148	156	154
																							50mm (2")	1/2T	-50	172	149	160	160
																							50mm (2")	1/2T	-76	127	146	132	135
																							50mm (2")	1/2T	-101	60	61	106	76
																			747	491	34	71	100mm (4")	1/2T	-46	168	142	158	156
																							100mm (4")	1/4T	-46	163	146	154	154

Fig. 4

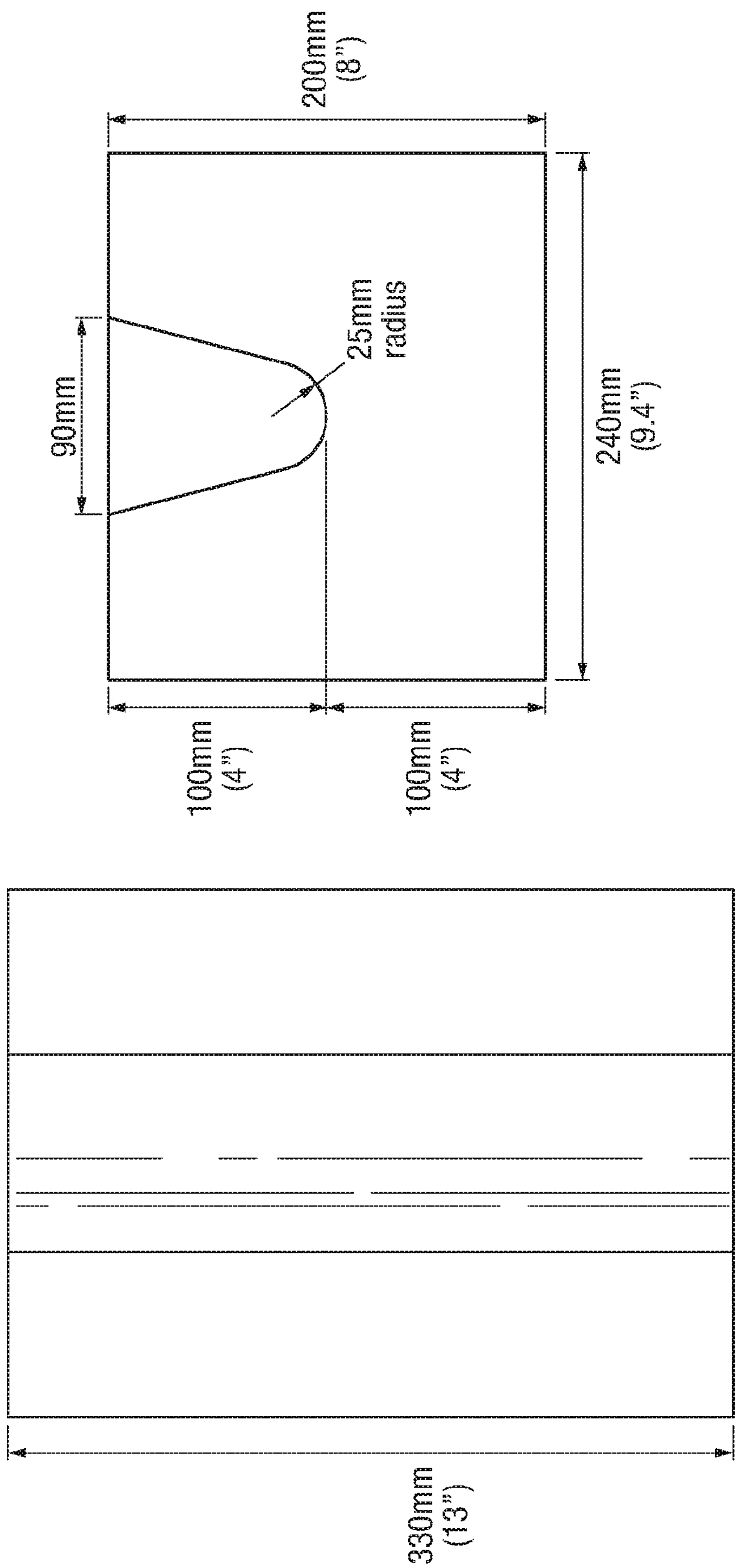
C %	Si %	Mn %	P %	S %	Cr %
0.01	0.29	0.69	0.024	0.0003	25.29

Mo %	Ni %	Cu %	N %	W %	Al %
3.58	9.24	0.57	0.22	0.63	0.013

Ti %	Sn %	Nb %	Co %	B %	V %
0.005	0.004	0.006	0.04	0.0023	0.08

Fig. 5

200mm Weld Test Plate Showing Machined Groove to 100mm Depth 25mm Radius



Dimensions of the 200mm Thick Weld Test Piece

Fig. 6

OPTION A - PWHT: As Welded

		Notch Location	Impact Results (Test Temperature -46°C)
		Notch location - weld cap centre line	186, 221, 189 av 199J
		Notch location - weld centre line (25mm deep)	175, 187, 175 av 179J
		Notch location - weld centre line (50mm deep)	146, 119, 142 av 136J
		Notch location - weld centre line (75mm deep)	153, 122, 151 av 142J
		Notch location - weld centre line (98.5mm Root)	180, 187, 151 av 173J

OPTION B - PWHT: 1120 / 1050°C

		Notch Location	Impact Results (Test Temperature -46°C)
		WELD CENTRE LINE RESULTS	
		Notch location - weld cap centre line	198, 194, 207 av 199J
		Notch location - weld centre line (50mm deep)	106, 104, 91 av 100J
		Notch location - weld centre line (98.5mm Root)	89, 102, 102 av 102J
		FUSION LINE RESULTS	
		Notch location Weld cap F/L	176, 186, 166 av 176J
		Notch location 50mm deep F/L	160, 189, 174 av 174J
		Notch location 98.5mm deep Root F/L	141, 165, 114 av 140J
		HAZ RESULTS	
		Notch location 50mm deep F/L + 3mm	160, 183, 165 av 169J
		Notch location 50mm deep F/L + 5mm	126, 139, 162 av 142J

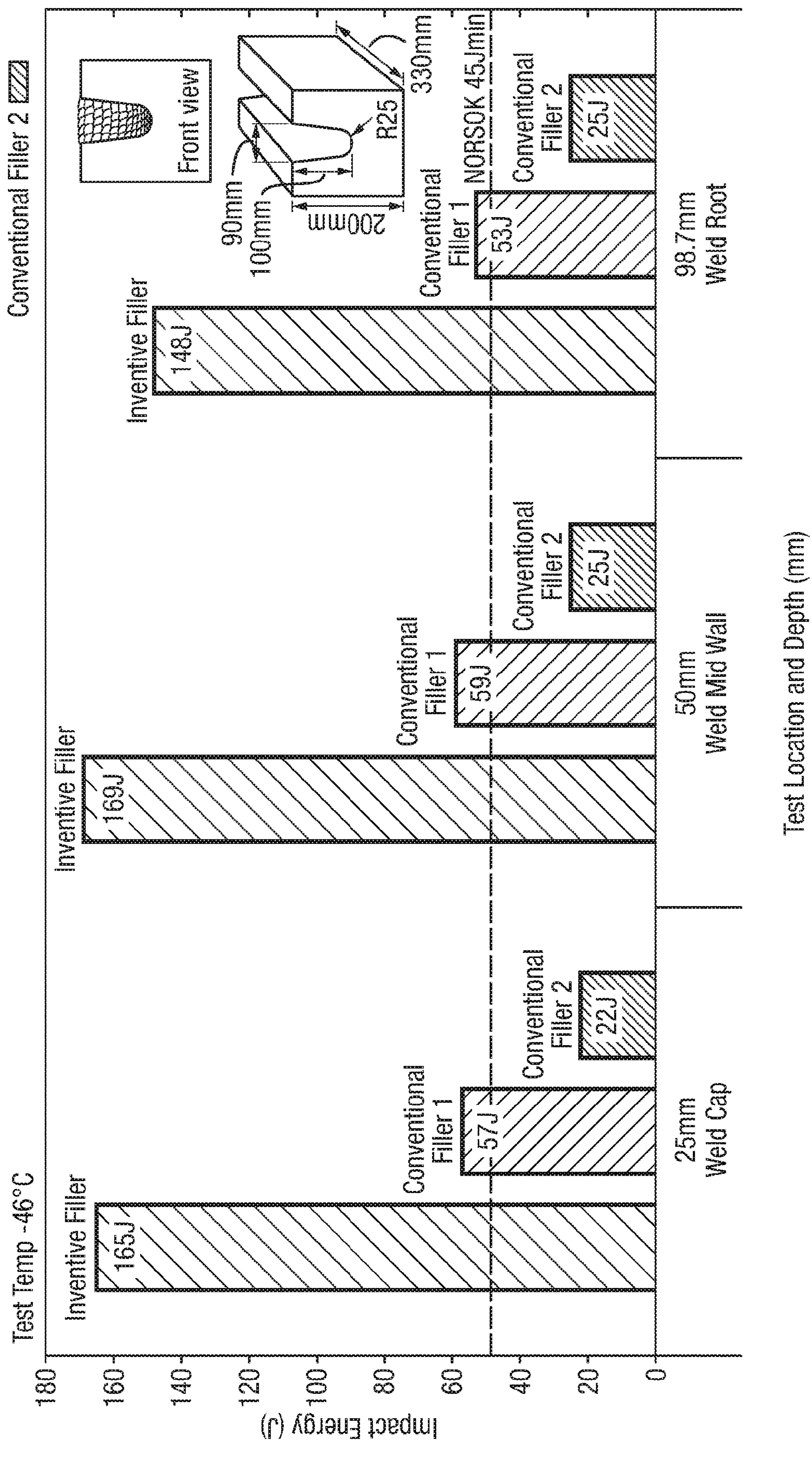
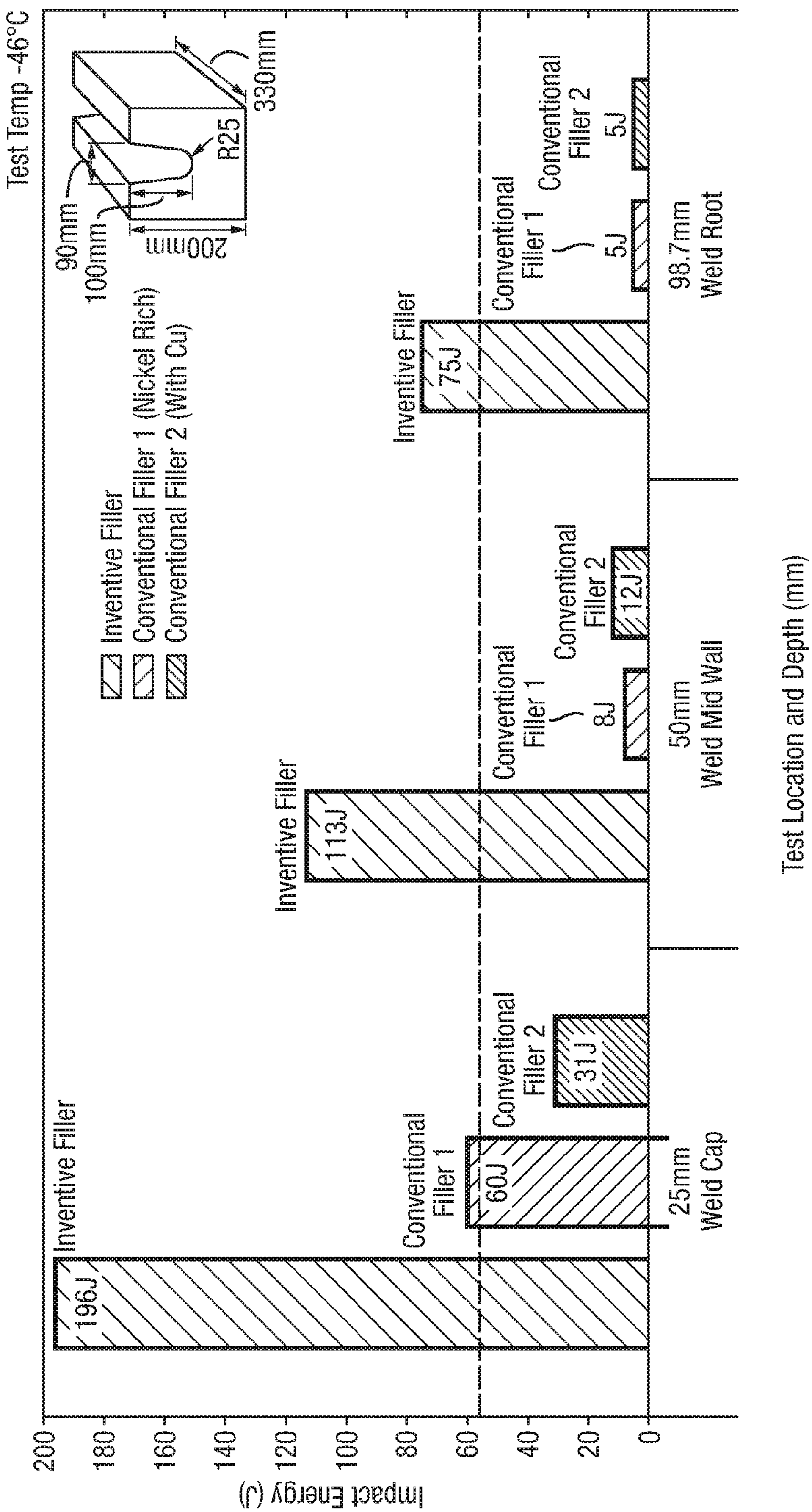

Inventive Filler
Conventional Filler 1
Conventional Filler 2
Test Temp -46°C
Front view
90mm
100mm
200mm
R25
330mm
NORSOK 45Jmin
165J
57J
22J
169J
59J
25J
148J
53J
25J
25mm Weld Cap
50mm Weld Mid Wall
98.7mm Weld Root
Test Location and Depth (mm)
Impact Energy (J)
180
160
140
120
100
80
60
40
20
0

Fig. 7

Fig. 8


Test Temp -46°C
90mm
100mm
200mm
R25
330mm
Inventive Filler
Conventional Filler 1 (Nickel Rich)
Conventional Filler 2 (With Cu)
Inventive Filler
196J
Conventional Filler 1
60J
Conventional Filler 2
31 J
25mm Weld Cap
Inventive Filler
113J
Conventional Filler 1
8J
Conventional Filler 2
12J
50mm Weld Mid Wall
Inventive Filler
75J
Conventional Filler 1
5J
Conventional Filler 2
5J
98.7mm Weld Root
Impact Energy (J)
200
180
160
140
120
100
80
60
40
20
0
Test Location and Depth (mm)

INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2016/054047

A. CLASSIFICATION OF SUBJECT MATTER

INV. C22C38/00 C22C38/02 C22C38/04 C22C38/06 C22C38/42
C22C38/44 C22C38/46 C22C38/48 C22C38/52 B23K35/30
C21D6/00 C21D9/50 C21D1/18

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C22C B23K C21D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	KR 2015 0074700 A (POSCO [KR]) 2 July 2015 (2015-07-02) the whole document -----	1-16,44
X	MEE VAN DER V ET AL: "HOW TO CONTROL HYDROGEN LEVEL IN (SUPER) DUPLEX STAINLESS STEEL WELDMENTS USING THE GTAW OR GMAW PROCESS", WELDING JOURNAL, AMERICAN WELDING SOCIETY, MIAMI, FL, US, vol. 78, no. 1, 1 January 1999 (1999-01-01), pages 7-S, XP000800822, ISSN: 0043-2296	1-21, 23-30,44
A	the whole document -----	22
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[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
24 April 2017	10/05/2017

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Vlassi, Eleni

INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2016/054047

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	KR 2014 0083169 A (POSCO [KR]) 4 July 2014 (2014-07-04) the whole document	1-16,44
X	US 2005/158201 A1 (PARK YONG-SOO [KR] ET AL) 21 July 2005 (2005-07-21) claims 1-17 tables 1-5 examples 1-11	1-16,44
X	TAVARES S S M ET AL: "Influence of heat treatments at 475 and 400 °C on the pitting corrosion resistance and sensitization of UNS S32750 and UNS S32760 superduplex stainless steels", MATERIALS AND CORROSION, WILEY, vol. 63, no. 6, 1 June 2012 (2012-06-01), pages 522-526, XP001577113, ISSN: 0947-5117, DOI: 10.1002/MACO.201006016 [retrieved on 2011-03-24] the whole document	1-16,44
X	DE MESSANO L V R ET AL: "The effect of biofouling on localized corrosion of the stainless steels N08904 and UNS S32760", INTERNATIONAL BIODETERIORATION & BIODEGRADATION, ELSEVIER, AMSTERDAM, NL, vol. 63, no. 5, 1 July 2009 (2009-07-01), pages 607-614, XP026139766, ISSN: 0964-8305, DOI: 10.1016/J.IBIOD.2009.04.006 [retrieved on 2009-05-07] the whole document	1-16,44
X	BARNOUSH AFROOZ ET AL: "Oxygen argon plasma treatment effect on hydrogen uptake in austenitic stainless steels", INTERNATIONAL JOURNAL OF HYDROGEN ENERGY, ELSEVIER SCIENCE PUBLISHERS B.V., BARKING, GB, vol. 39, no. 26, 25 July 2014 (2014-07-25) , pages 14120-14131, XP029046913, ISSN: 0360-3199, DOI: 10.1016/J.IJHYDENE.2014.06.161 the whole document	1-16,44
X A	US 6 129 999 A (UEDA MASAKATSU [JP] ET AL) 10 October 2000 (2000-10-10) table 2 claims 1-4	17-23, 25-30,44 1-16,24

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INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2016/054047

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4 765 953 A (HAGENFELDT CARL P U [SE] ET AL) 23 August 1988 (1988-08-23) claims 1-8 column 5 - column 7 -----	1-16,44
A	WO 2013/064746 A1 (OUTOKUMPU OY [FI]) 10 May 2013 (2013-05-10) claims 1-14 page 9 - page 14 -----	1-16,44
A	US 4 816 085 A (FLASCHE LEE H [US] ET AL) 28 March 1989 (1989-03-28) claims 1-5 tables 1-2 -----	1-30,44
A	US 2013/316193 A1 (NAGAYAMA HIROYUKI [JP] ET AL) 28 November 2013 (2013-11-28) claims 1-16 tables 1-4 -----	1-30,44
A	EP 0 867 256 A1 (SUMITOMO METAL IND [JP]; SUMIKIN WELDING IND LTD [JP]) 30 September 1998 (1998-09-30) tables 1-10 claims 1-5 -----	1-30,44
A	EP 2 832 487 A1 (NIPPON STEEL & SUMITOMO METAL CORP [JP]) 4 February 2015 (2015-02-04) table 3 claims 1-9 -----	1-30,44
A	JP S58 93593 A (SUMITOMO METAL IND) 3 June 1983 (1983-06-03) the whole document -----	1-30,44

INTERNATIONAL SEARCH REPORT

International application No.
PCT/GB2016/054047

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.

3. ☒ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

1-30, 44

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☒ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1-16(completely); 44(partially)

   a steel including, in mass %: 0.005 to 0.015% carbon; 0.05 to 0.35% silicon, 7.45 to 8.4% nickel; 1.00% or less manganese; 0.025% or less sulphur; 0.030% or less phosphorous; 24.0 to 26.0% chromium; 0.50 to 1.00% copper; 3.0 to 4.0% molybdenum; 0.010% or less niobium; 0.75% or less cobalt; 0.015% or less aluminium; 0.20 to 0.30% nitrogen; 0.50 to 0.85% tungsten; the balance being iron and incidental impurities, as well as , a cast, forged or wrought product made of said steel.

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2. claims: 17-30(completely); 44(partially)

   a welding consumable including, in mass %: 0.015% or less carbon; 0.05 to 0.35% silicon, 7.45 to 10.5% nickel; 2.00% or less manganese; 0.025% or less sulphur; 0.030% or less phosphorous; 24.0 to 27.0% chromium; 0.00 to 1.00% copper; 3.0 to 4.5% molybdenum; 0.75% or less cobalt; 0.010% or less niobium; 0.015% or less aluminium; 0.20 to 0.30% nitrogen; 0.00 to 1.00% tungsten; the balance being iron and incidental impurities.

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3. claims: 31-38(completely); 45(partially)

   A method of welding a base steel using the welding consumable of claims 17-30.

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4. claims: 39-43(completely); 45(partially)

   a method of heat treating a cast or forged or wrought of a duplex stainless steel in the welded or unwelded condition, comprising: raising the temperature of the product to a first temperature between 1100 and 1150 C and holding at the first temperature; lowering the temperature of the product to a second temperature between 1040 and 1070 C and holding at the second temperature; and quenching the product in water from the second temperature.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/GB2016/054047

Patent document cited in search report		Publication date	Patent family member(s)			Publication date
KR 20150074700	A	02-07-2015	NONE			
KR 20140083169	A	04-07-2014	NONE			
US 2005158201	A1	21-07-2005	AU	2003221202	A1	08-10-2003
			CN	1643176	A	20-07-2005
			CN	101580917	A	18-11-2009
			DE	60313763	T2	24-01-2008
			EP	1495150	A1	12-01-2005
			EP	1803832	A1	04-07-2007
			JP	4834292	B2	14-12-2011
			JP	2005520934	A	14-07-2005
			JP	2011174183	A	08-09-2011
			KR	20030077239	A	01-10-2003
			US	2005158201	A1	21-07-2005
			WO	03080886	A1	02-10-2003
US 6129999	A	10-10-2000	AU	703877	B2	01-04-1999
			CA	2233338	A1	03-04-1997
			DE	69628190	D1	18-06-2003
			DE	69628190	T2	20-11-2003
			DK	0864663	T3	15-09-2003
			EP	0864663	A1	16-09-1998
			JP	3427387	B2	14-07-2003
			NO	981373	A	28-05-1998
			US	6129999	A	10-10-2000
			WO	9712072	A1	03-04-1997
US 4765953	A	23-08-1988	AT	77660	T	15-07-1992
			AU	586024	B2	29-06-1989
			BR	8604259	A	05-05-1987
			CA	1283795	C	07-05-1991
			DE	3685795	D1	30-07-1992
			DE	3685795	T2	24-12-1992
			DK	422586	A	06-03-1987
			EP	0220141	A2	29-04-1987
			JP	H0826435	B2	13-03-1996
			JP	S6256556	A	12-03-1987
			NO	863541	A	06-03-1987
			SE	453838	B	07-03-1988
			US	4765953	A	23-08-1988
			ZA	8606550	B	29-04-1987
WO 2013064746	A1	10-05-2013	CN	103975088	A	06-08-2014
			EP	2773785	A1	10-09-2014
			FI	20110384	A	05-05-2013
			JP	5870201	B2	24-02-2016
			JP	2014532811	A	08-12-2014
			TW	201323629	A	16-06-2013
			US	2015050180	A1	19-02-2015
			WO	2013064746	A1	10-05-2013
US 4816085	A	28-03-1989	BR	8804092	A	07-03-1989
			CA	1332673	C	25-10-1994
			CH	675430	A5	28-09-1990
			GB	2208655	A	12-04-1989
			IT	1226737	B	05-02-1991
			JP	H01132741	A	25-05-1989

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/GB2016/054047

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
		US 4816085 A	28-03-1989
US 2013316193 A1	28-11-2013	AU 2012218659 A1	05-09-2013
		CA 2827103 A1	23-08-2012
		CN 103370166 A	23-10-2013
		EP 2676763 A1	25-12-2013
		JP 5013030 B1	29-08-2012
		US 2013316193 A1	28-11-2013
		WO 2012111535 A1	23-08-2012
EP 0867256 A1	30-09-1998	DE 69709308 D1	31-01-2002
		DE 69709308 T2	08-08-2002
		EP 0867256 A1	30-09-1998
		NO 982150 A	13-07-1998
		WO 9810888 A1	19-03-1998
EP 2832487 A1	04-02-2015	AU 2013241368 A1	02-10-2014
		CA 2867673 A1	03-10-2013
		CN 104245211 A	24-12-2014
		EP 2832487 A1	04-02-2015
		JP 5382266 B1	08-01-2014
		JP 5751292 B2	22-07-2015
		JP 2014000607 A	09-01-2014
		JP WO2013146860 A1	14-12-2015
		US 2015056005 A1	26-02-2015
		WO 2013146860 A1	03-10-2013
JP S5893593 A	03-06-1983	NONE	