(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 1 722 002 A1

(12) EUROPEAN PATENT APPLICATION

(43) Date of publication:
15.11.2006 Bulletin 2006/46

(51) Int Cl.:
C22C 38/44 $^{(2006.01)}$

(21) Application number: **06113879.8**

(22) Date of filing: **02.09.2002**

(84) Designated Contracting States:
AT BE BG CH CY CZ DE DK EE ES FI FR GB GR IE IT LI LU MC NL PT SE SK TR

(30) Priority: **02.09.2001 SE 0102931**

(62) Document number(s) of the earlier application(s) in accordance with Art. 76 EPC:
02763168.8 / 1 423 548

(71) Applicant: **Sandvik Intellectual Property AB
811 81 Sandviken (SE)**

(72) Inventors:
- **SUNDSTRÖM, Ann
S-818 42 Forsbacka (SE)**
- **NYSTRÖM, Anna-Lena
S-811 32 Sandviken (SE)**
- **KANGAS, Pasi
S-811 36 Sandviken (SE)**

Remarks:
This application was filed on 12 - 05 - 2006 as a divisional application to the application mentioned under INID code 62.

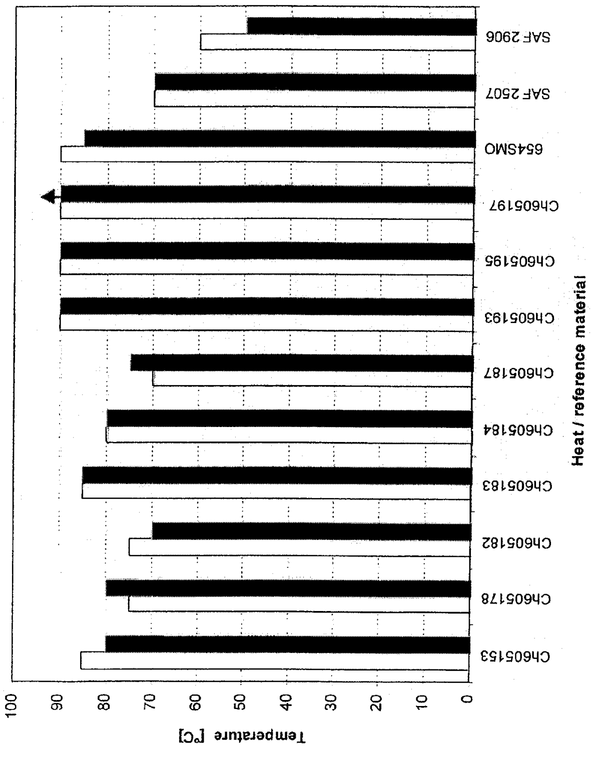
(54) Duplex steel alloy

(57) The present invention relates to a duplex stainless steel alloy, with high resistance to corrosion in combination with good structural stability and hotworkability. The duplex stainless steel has the following composition in percent by weight:

C	max 0,03%
Si	max 0,5%
Mn	0 - 3,0%
Cr	24,0 - 30,0%
Ni	4,9 - 10,0%
Mo	3,0 - 5,0%
N	0,28 - 0,5%
B	0 - 0,0030%
S	max 0,010%
W	0 - 3,0%
Cu	0 - 2,0%
Ru	0 - 0,3%
Al	0 - 0,03%
Ca	0 - 0,010%
Ti	0 - 0,35 %
V	0 - 0,55 %

balance Fe and normal occurring impurities

Figure 1



EP 1 722 002 A1

Printed by Jouve, 75001 PARIS (FR)

Description

TECHNICAL FIELD OF THE INVENTION

[0001] The present invention relates to a stainless steel alloy, closer determined a duplex stainless steel alloy with ferritic-austenitic matrix and with high resistance to corrosion in combination with good structural stability and hotworkability, particularly a duplex stainless steel with a content of ferrite of 40-65 volume-% and a well balanced composition, which imparts the material corrosion properties, which make it more suitable for use in chloride-containing environments than earlier been considered being possible.

BACKGROUND OF THE INVENTION

[0002] Over the recent years, the environments in which corrosion resistant metallic materials were used, became more aggressive, the requirements on the corrosion properties as well as on their mechanical properties increased. Duplex steel alloys, which were established as an alternative to until that used steel grades, as for example high alloyed austenitic steels, nickel-base alloys or other high alloyed steels, are not exempted from this development.
An established measure for the corrosion resistance in chloride-containing environments is the so-called Pitting Resistance Equivalent (abbreviated PRE), which is defined as

$$\mathrm{PRE}=\%\mathrm{Cr}+3{,}3\%\mathrm{Mo}+16\%\mathrm{N}$$

where the percentages for each element allude to weight-percent.
A higher numerical value indicates a better corrosion resistance in particular against pitting corrosion. The essential alloying elements, which affect this property, are according to the formula Cr, Mo, N. An example for such a steel grade is evident from EP0220141, which hereby through this reference is included in this description. This steel grade with the denotation SAF2507 (UNS S32750) was mainly alloyed with high contents of Cr, Mo and N. It is consequently developed against this property with above all good resistance to corrosion in chloride environments.

[0003] In recent times also the elements Cu and W have shown to be efficient alloying additions for further optimization of the steel's corrosion properties in chloride environments. The element W has by then been used as substitute for a portion of Mo, as for example in the commercial alloy DP3W (UNS S39274) or Zeron100, which contain 2,0% respectively 0,7% W. The later contains even 0,7% Cu with the purpose to increase the corrosion resistance of the alloy in acid environments.

[0004] The alloying addition of tungsten led to a further development of the measure for the corrosion resistance and thereby the PRE-formula to the PREW-formula, which also makes the relationship between the influence of Mo and W on the alloys corrosion resistance clearer:

$$\mathrm{PREW}=\%\mathrm{Cr}+3{,}3(\%\mathrm{Mo}+0{,}5\%\mathrm{W})+16\%\mathrm{N},$$

such as described for example in EP 0 545 753. This publication refers to a duplex stainless alloy with generally improved corrosion properties.
The above-described described steel grades have a PRE-number, irrespective method of calculation, which lies above 40.

[0005] From the alloys with good corrosion resistance in chloride environments also SAF 2906 shall be mentioned, which composition appears from EP 0 708 845. This alloy, which is characterized by higher contents of Cr and N compared to for example SAF2507, has shown being especially suitable for use in environments, where resistance to intergranular corrosion and corrosion in ammonium carbamate is of importance, but it has also a high corrosion resistance in chloride-containing environments.

[0006] US-A-4 985 091 describes an alloy intended for use in hydrochloric and sulfuric acid environments, where mainly intergranular corrosion arises. It is primarily intended as alternative to recently used austenitic steels.

[0007] US-A-6 048 413 describes a duplex stainless alloy as alternative to austenitic stainless steels, intended for use in chloride-containing environments.

[0008] The disadvantage with the above-described alloys, all with high PRE-numbers, is the appearance of hard and brittle intermetallic precipitations in the steel, as for example sigma phase, especially after heat-treating, such as for example by welding under later processing. That results in a harder material with poorer workability and finally a deteriorated corrosion resistance.

[0009] In order to further improve among others the pitting corrosion resistance of duplex stainless steels, an increase of the PRE-number in both the ferrite phase and the austenite phase is required, without for that sake jeopardizing the structural stability or workability of the material. If the composition in the two phases is not equivalent with regard to the active alloying components, one phase becomes more sensitive for pitting and crevice corrosion. Consequently, the phase which is more sensitive to corrosion controls the resistance of the alloy, while the structural stability is controlled by the highest alloyed phase.

SUMMARY OF THE INVENTION

[0010] It is therefore an object of the present invention to provide a duplex stainless steel alloy, which shows high corrosion resistance in combination with improved mechanical properties and which is most appropriate for use in environments where a high resistance to general corrosion and localized corrosion is required, such as for example in chloride-containing environments.

[0011] It is another object of the present invention to provide a duplex stainless steel alloy with a content of ferrite in the range of 40 to 65 volume-% and a PRE-number of at least between 46 and 50 in both the austenite and ferrite phase and with an optimum relationship between PRE austenite and PRE ferrite in the range of 0,90 to 1,15; preferably between 0,9 and 1,05.

[0012] It is a further object of the present invention to provide a duplex stainless steel alloy with a Critical Pitting Corrosion Temperature (henceforth abbreviated CPT) value higher than 90ºC, preferably higher than 95ºC and a Critical Crevice-corrosion Temperature (henceforth abbreviated CCT) value of lowest 50ºC in 6% $FeCl_3$, preferably at least 60ºC in 6% $FeCl_3$.

[0013] It is a further object of the present invention to provide an alloy with impact strength of at least 100 J at room temperature and an elongation after tensile test of at least 25% at room temperature.

[0014] For its high alloying content, the material according to the present invention shows remarkably good workability, in particular hotworkability and shall thereby be very suitable to be used for example the production of bars, tubes, such as welded and seamless tubes, plate, strip, wire, welding wire, constructive parts, such as for example pumps, valves, flanges and couplings.

[0015] These objects are fulfilled according to the present invention with duplex stainless steel alloys, which contain (in weight-%) up to 0,03% C, up to 0,5% Si, 24,0-30,0% Cr, 4,9-10,0% Ni, 3,0-5,0% Mo, 0,28-0,5% N, 0-3,0% Mn, 0-0,0030% B, up to 0,010% S, 0-0,03% Al, 0-0,010% Ca, 0-3,0% W, 0-2,0% Cu, 0-3,5% Co, 0-0,3% Ru, balance Fe and inevitable impurities.

SHORT DESCRIPTION OF THE DRAWINGS

[0016]

Figure 1 shows CPT-values from tests of the test heats in the modified ASTM G48C test in "Green Death"-solution compared with the duplex steels SAF2507, SAF 2906 as well as the high alloyed austenitic steel 654SMO.

Figure 2 shows CPT-values attained with the help of the modified ASTM G48C test in "Green Death"-solution for the test heats compared with the duplex steel SAF2507 as well as the austenitic steel 654SMO.

Figure 3 shows the average amount of erosion in mm/year in 2%HCl at a temperature of 75°C.

Figure 4 shows the results from hot ductility testing for most of the heats.

DETAILED DESCRIPTION OF THE INVENTION

[0017] A systematic development work has surprisingly shown that one by means of a well-balanced combination of the elements Cr, Mo, Ni, N, Mn and Co can obtain optimal dispensation of the elements in the ferrite and austenite, which enables a very corrosion resistant material with only an insignificant amount of sigma phase in the material. The material obtains also good workability, which enables extruding to seamless tubes. It shows that with the intention to obtain a combination of high corrosion resistance in connection with good structural stability a much narrow combination of the alloying elements in the material is required. The alloy according to the invention contains (in weight-%):

C	Max 0,03%
Si	Max 0,5%
Mn	0 - 3,0%
Cr	24,0 - 30,0%
Ni	4,9 - 10,0%

(continued)

Mo	3,0 - 5,0%
N	0,28 - 0,5%
B	0-0,0030%
S	max 0,010%
Co	0-3,5%
W	0-3,0%
Cu	0-2,0%
Ru	0-0,3%
Al	0-0,03%
Ca	0-0,010%

balance Fe and normal occurring impurities and additions, whereby the content of ferrite is 40-65 volume-%.

[0018] Carbon (C) has limited solubility in both ferrite and austenite. The limited solubility implies a risk of precipitation of chromium carbides and the content should therefore not exceed 0,03 weight-%, preferably not exceed 0,02 weight-%.

[0019] Silicon (Si) is utilized as desoxidation agent in the steel production as well as it increases the flowability during production and welding. However, too high contents of Si lead to precipitation of unwanted intermetallic phase, wherefore the content is limited to max 0,5 weight-%, preferably max 0,3 weight-%.

[0020] Manganese (Mn) is added in order to increase the N-solubility in the material. However, it has shown that Mn only has a limited influence on the N-solubility in the type of alloy in question. Instead there are found other elements with higher influence on the solubility. Besides, Mn in combination with high contents of sulfur can give rise to formation of manganese sulfides, which act as initiation-points for pitting corrosion. The content of Mn should therefore be limited to between 0-3,0 weight-%, preferably 0,5-1,2 weight-%.

[0021] Chromium (Cr) is a much active element in order to improve the resistance to a majority of corrosion types. Furthermore, a high content of chromium implies that one gets a very good N-solubility in the material. Thus, it is desirable to keep the Cr-content as high as possible in order to improve the corrosion resistance. For very good amounts of corrosion resistance the content of chromium should be at least 24,0 weight-%, preferably 27,0 -29,0 weight-%. However, high contents of Cr increase the risk for intermetallic precipitations, for what reason the content of chromium must be limited up to max 30,0 weight-%.

[0022] Nickel (Ni) is used as austenite stabilizing element and is added in suitable contents in order to obtain the desired content of ferrite. In order to obtain the desired relationship between the austenitic and the ferritic phase with between 40-65 volume-% ferrite, an addition of between 4,9-10,0 weight-% nickel, preferably 4,9-8,0 weight-%, is required.

[0023] Molybdenum (Mo) is an active element which improves the resistance to corrosion in chloride environments as well as preferably in reducing acids. A too high Mo-content in combination with that the Cr-contents are high, implies that the risk for intermetallic precipitations increases. The Mo-content in the present invention should lie in the range of 3,0-5,0 weight-%, preferably 3,6-4,7 weight-%, in particular 4,0-4,3 weight-%.

[0024] Nitrogen (N) is a very active element, which increases the corrosion resistance, the structural stability as well as the strength of the material. Further, a high N-content improves the recovering of the austenite after welding, which gives good properties within the welded joint. In order to obtain a good effect of N, at least 0,28 weight-% N should be added. At high contents of N the risk for precipitation of chromium nitrides increases, especially when simultaneously the chromium content is high. Further, a high N-content implies that the risk for porosity increases because of the exceeded solubility of N in the smelt For these reasons the N-content should be limited to max 0,5 weight-%, preferably >0,35 - 0,45 weight-% N is added.

[0025] Boron (B) is added in order to increase the hotworkability of the material. At a too high content of Boron the weldability as well as the corrosion resistance could deteriorate. Therefore, the content of boron should be limited to 0,0030 weight-%.

[0026] Sulfur (S) influences the corrosion resistance negatively by forming soluble sulfides. Further, the hot workability detoriates, for what reason the content of sulfur is limited to max 0,010 weight-%.

[0027] Cobalt (Co) is added in order to improve foremost the structural stability as well as the corrosion resistance. Co is an austenite-stabilizing element. In order to obtain effect should at least 0,5 weight-%, preferably at least 1,5 weight-% be added. Because cobalt is a relatively expensive element, the addition of cobalt is therefor limited to max 3,5 weight-%.

[0028] Tungsten increases the resistance to pitting- and crevice corrosion. But the addition of too high contents of tungsten in combination with that the Cr-contents as well as Mo-contents are high, means that the risk for intermetallic precipitations increases. The W-content in the present invention should lie in the range of 0-3,0 weight-%, preferably between 0,5 and 1,8 weight-%.

[0029] Copper is added in order to improve the general corrosion resistance in acid environments such as sulfuric acid. At the same time Cu influences the structural stability. However, high contents of Cu imply that the solid solubility will be exceeded. Therefor the Cu-content should be limited to max 2,0 weight-%, preferably between 0,5 and 1,5 weight-%.

[0030] Ruthenium (Ru) is added in order to increase the corrosion resistance. Because ruthenium is a very expensive element, the content should be limited to max 0,3 weight-%, preferably more than 0 and up to 0,1 weight-%.

[0031] Aluminum (Al) and Calcium (Ca) are used as desoxidation agents at the steel production. The content of Al should be limited to max 0,03 weight-% in order to limit the forming of nitrides. Ca has a favorable effect on the hotductility. However, the Ca-content should be limited to 0,010 weight-% in order to avoid an unwanted amount of slag.

[0032] The content of ferrite is important in order to obtain good mechanical properties and corrosion properties as well as good weldability. From a corrosion point of view and a point of view of weldability a content of ferrite between 40-65% is desirable in order to obtain good properties. Further, high contents of ferrite imply that the impact strength at low temperatures as well as the resistance to hydrogen-induced brittleness risks deteriorating. The content of ferrite is therefore 40-65 volume-%, preferably 42-60 volume-%, in particular 45-55 volume-%.

DESCRIPTION OF PREFERED EMBODIEMENTS

[0033] In the examples below the composition of a number of test heats is presented, which illustrate the effect of different alloying elements on the properties. Heat 605182 represents a reference composition and is consequently not a part of the field of this invention. Neither shall the remaining heats be considered limiting the invention, without only specifying examples of heats, which illustrate the invention according to the claims.

The specified PRE-numbers or -values consider always amounts calculated according to the PREW-formula, even though this is not explicitly mentioned.

EXAMPLE 1

[0034] The test heats according to this example were produced by casting of 170kg ingots in the laboratory, which were hotforged to round bars. Those were hotextruded to bars (round bars as well as flat bars), where test material was taken out from the round bars. Further on the flat bars were annealed before cold rolling took place, whereafter further test material was taken out. From a material engineering point of view, the process can be considered to be representative for the preparation in bigger scale, for example for the production of seamless tubes by the extrusion method, followed by cold rolling. Table 1 shows the composition of the first batch of test heats.

Table 1. Composition for test heats, weight-%.

Heat	Mn	Cr	Ni	Mo	W	Co	V	La	Ti	N
605193	1,03	27,90	8,80	4,00	0,01	0,02	0,04	0,01	0,01	0,36
605195	0,97	27,90	9,80	4,00	0,01	0,97	0,55	0,01	0,35	0,48
605197	1,07	28,40	8,00	4,00	1,00	1,01	0,04	0,01	0,01	0,44
605178	0,91	27,94	7,26	4,01	0,99	0,10	0,07	0,01	0,03	0,44
605183	1,02	28,71	6,49	4,03	0,01	1,00	0,04	0,01	0,04	0,28
605184	0,99	28,09	7,83	4,01	0,01	0,03	0,54	0,01	0,01	0,44
605187	2,94	27,74	4,93	3,98	0,01	0,98	0,06	0,01	0,01	0,44
605153	2,78	27,85	6,93	4,03	1,01	0,02	0,06	0,02	0,01	0,34
605182	0,17	23,48	7,88	5,75	0,01	0,05	0,04	0,01	0,10	0,26

[0035] In purpose to investigate the structural stability samples from every heat were annealed at 900-1150°C with steps of 50°C as well as they were quenched in air, respective water. At the lowest temperatures intermetallic phase was formed. The lowest temperature, where the amount of intermetallic phase became insignificant, was determined with the help of studies in light optical microscope. New samples from respective heat were annealed afterwards at said temperature under five minutes, whereafter the samples were cooled down with the constant cooling rate of -140°C/min to room temperature. Subsequently, the area fraction of sigma phase in the materials was determined with digital scanning of the pictures with back-scattering electrons in a scanning electron microscope. The results appear from Table 2.

[0036] T_{max} sigma was calculated with Thermo-Calc (TC version N thermodynamic database for steel TCFE99) based on characteristic amounts for all specified elements in the different variations. T_{max} sigma is the dissolving temperature for the sigma phase, where high dissolving temperatures indicate lower structural stability.

Table 2.

Heat	Heat treatment	Amount σ [vol-%]	Tmax σ
605193	1100°C, 5min	7,5%	1016
605195	1150°C, 5min	32%	1047
605197	1100°C, 5min	18%	1061
605178	1100°C, 5min	14%	1038
605183	1050°C, 5min	0,4%	997
605184	1100°C, 5min	0,4%	999
605187	1050°C, 5min	0,3%	962
605153	1100°C, 5min	3,5%	1032
605182	1100°C, 5min	2,0%	1028

[0037] The purpose of this investigation is to be able to rank the material with regard to the structural stability, i.e. this is not the real content of sigma phase in the samples, which were heat treated and quenched before for example the corrosion testing. One can see that T_{max} sigma, which was calculated with Thermo-Calc does not directly coincide with the measured amounts of sigma phase, however it is distinct that the test heats with the lowest calculated T_{max} sigma contain the lowest amount sigma phase during this investigation.

[0038] The pitting corrosion properties of all heats were tested for ranking in the so-called "Green Death"-solution, which consists of 1 %$FeCl_3$, 1 %$CuCl_2$, 11 % H_2SO_4, 1,2% HCl. The test procedure is equivalent to the pitting corrosion testing according to ASTM G48C, however, it will be carried out in the more aggressive "Green Death"-solution. Further, some of the heats were tested according to ASTMG48C (2 tests per heat). Also the electrochemical testing in 3%NaCl (6 tests per heat) was carried out. The results in form of the Critical Pitting Temperature (CPT) from all tests appear from Table 3, such as the PREW-number (Cr+3,3(Mo+0,5W)+16N) for the total composition of the alloy as well as for austenite and ferrite. The indexing alpha refers to the ferrite and gamma refers to the austenite.

Table 3.

Heat	PRE α	PRE γ	PRE γ/ PRE α	PRE	CPT °C Modified ASTM G48C Green death	CPT °C ASTM G48 C 6% $FeCl_3$	CPT °C 3% NaCl
605193	51,3	49,0	0,9552	46,9	90/90		64
605195	51,5	48,9	0,9495	48,7	90/90		95
605197	53,3	53,7	1,0075	50,3	90/90	>95	>95
605178	50,7	52,5	1,0355	49,8	75/80		94
605183	48,9	48,9	1,0000	46,5	85/85	90	93
605184	48,9	51,7	1,0573	48,3	80/80		72
605187	48,0	54,4	1,1333	48,0	70/75		77
605182	54,4	46,2	0,8493	46,6	75/70	85	62
654SMO					90/85		
SAF2507					70/70		
SAF2609					60/50		
605153	49,6	51,9	1,0464	48,3	8085	85	90

[0039] It is established that there exists a linear ratio between the lowest PRE-number in the austenite or ferrite and the CPT-value in the duplex steel, but the results in Table 3 show that the PRE-number not solely explains the CPT-values. In Figure 1 the CPT-values from test in the modified ASTM G48C test are shown diagrammatically. The duplex steels SAF2507, SAF2906 as well as the high alloyed austenitic steel 654SMO are included as reference. It is distinct from these results that all test materials show better CPT in the modified ASTM G48C than SAF2507 as well as SAF2906. Furthermore some of the test materials show CPT results in the modified ASTM G48C at the same level as or in excess of 654SMO. The test heat 605183, alloyed with cobalt shows good structural stability at a controlled cooling rate of (-140°C/min) in spite that it contains high contents of chromium as well as of molybdenum, shows better results than SAF2507 and SAF2906. It appears from this investigation that a high PRE does not solely explain the CPT values, without the relationship PRE austenit/PRE ferrite is of extreme weight for the properties of the higher alloyed duplex steels, and a very narrow and exact leveling between the alloying elements is required in order to obtain this optimum ratio, which lies between 0,9-1,15; preferably 0,9-1,05 and simultaneously obtain PRE values of above 46. The relationship PRE austenit/PRE ferrite against CPT in the modified ASTM G48C test for the test heats is given in Table 3.

[0040] The strength at room temperature (RT), 100°C and 200°C and the impact strength at room temperature (RT) have been determined for all heats and is shown as average amount for three tests.

[0041] Tensile test specimen (DR-5C50) were manufactured from extruded bars, Ø 20mm, which were heattreated at temperatures according to Table 2 in 20 minutes followed by cooling down in either air or water (605195, 605197, 605184). The results of the tests are presented in Table 4 and 5. The results of the tensile test show that the contents of chromium, nitrogen and tungsten strongly influence the impact strength of the material. Besides 605153, all heats fulfill the requirement of a 25% elongation at tensile testing at room temperature (RT).

Table 4. Impact strength

Heat	Temperature	$R_{p0,2}$	$R_{p1,0}$	R_m	A5	Z
		(MPa)	(MPa)	(MPa)	(%)	(%)
605193	RT	652	791	916	29,7	38
	100ºC	513	646	818	30,4	36
	200ºC	511	583	756	29,8	36
605195	RT	671	773	910	38,0	66
	100ºC	563	637	825	39,3	68
	200ºC	504	563	769	38,1	64
605197	RT	701	799	939	38,4	66
	100ºC	564	652	844	40,7	69
	200ºC	502	577	802	35,0	65
605178	RT	712	828	925	27,0	37
	100ºC	596	677	829	31,9	45
	200ºC	535	608	763	27,1	36
605183	RT	677	775	882	32,4	67
	100ºC	560	642	788	33,0	59
	200ºC	499	578	737	29,9	52
605184	RT	702	793	915	32,5	60
	100ºC	569	657	821	34,5	61
	200ºC	526	581	774	31,6	56
605187	RT	679	777	893	35,7	61
	100ºC	513	628	799	38,9	64
	200ºC	505	558	743	35,8	58
605153	RT	715	845	917	20,7	24

(continued)

Heat	Temperature	$R_{p0,2}$	$R_{p1,0}$	R_m	A5	Z
		(MPa)	(MPa)	(MPa)	(%)	(%)
	100ºC	572	692	817	29,3	27
	200ºC	532	611	749	23,7	31
605182	RT	627	754	903	28,4	43
	100ºC	493	621	802	31,8	42

Table 5. Impact Strength

Heat	Annealing [°C/min]	Cooling	Impact strength [J]	Annealing [°C/min]	Cooling	Impact strength [J]
605193	1100/20	Air	35	1100/20	Water	242
605195	1150/20	Water	223			
605197	1100/20	Water	254	1130/20	Water	259
605178	1100/20	Air	62	1100/20	Water	234
605183	1050/20	Air	79	1050/20	Water	244
605184	1100/20	Water	81	1100/20	Air	78
605187	1050/20	Air	51	1100/20	Water	95
605153	1100/20	Air	50	1100/20	Water	246
605182	1100/20	Air	22	1100/20	Water	324

This investigation shows very distinct that water quenching is certainly necessary in order to obtain the best structure and consequently good values for the impact strength. The requirement is 100J at test at room temperature and all heats pass this, except heat 605184 and 605187, where certainly the latter lies very near the requirement.

[0042] Table 6 shows the results from the Tungsten-Inert-Gas remelting test (henceforth-abbreviated TIG), where the heats 605193, 605183, 605184 as well as 605253 show a good structure in the heat affected zone (Heat Affected Zone, henceforth-abbreviated HAZ). The Ti- containing heats show Tin in HAZ. A too high chromium- and nitrogen content results in precipitation of Cr_2 N, which shall be avoided because it detoriates the properties of the material.

Table 6.

Heat	Precipitations Protective gas Ar (99,99%)
605193	HAZ: OK
605195	HAZ: Large amounts of TIN and σ-phase
605197	HAZ: Small amounts of Cr_2N in δ-grains, but not much
605178	HAZ: Cr_2N in δ-grains, otherwise OK
605183	HAZ: OK
605184	HAZ: OK
605187	HAZ: Cr_2N quite near the meltingbond, no precipitations farther out
605153	HAZ: OK
605182	HAZ: TiN and decorated grainboundaries δ/δ

EXAMPLE 2

[0043] In the below-mentioned example the composition of a further number of test heats produced with the purpose to find the optimum composition is given. These heats are modified starting out from the properties of the heats with good structural stability as well as high corrosion resistance, from the results, which were shown in example 1. All heats in Table 7 are included in the composition according to the present invention, where heats 1-8 are included into a statistical test model, while the heats e to n are additional test alloys within the scope of this invention.

[0044] A number of test heats were produced by casting of 270kg ingots, which were hotforged to round bars. Those were extruded to bars, wherefrom test samples were taken. Afterwards the bar was annealed before cold rolling to flat bars was executed, after that further test material was taken out. Table 7 shows the composition for these test heats.

Table 7.

	Heat	Mn	Cr	Ni	Mo	W	Co	Cu	Ru	B	N
1	605258	1,1	29,0	6,5	4,23		1,5			0,0018	0,46
2	605249	1,0	28,8	7,0	4,23		1,5			0,0026	0,38
3	605259	1,1	29,0	6,8	4,23		0,6			0,0019	0,45
4	605260	1,1	27,5	5,9	4,22		1,5			0,0020	0,44
5	605250	1,1	28,8	7,6	4,24		0,6			0,0019	0,40
6	605251	1,0	28,1	6,5	4,24		1,5			0,0021	0,38
7	605261	1,0	27,8	6,1	4,22		0,6			0,0021	0,43
8	605252	1,1	28,4	6,9	4,23		0,5			0,0018	0,37
e	605254	1,1	26,9	6,5	4,8		1,0			0,0021	0,38
f	605255	1,0	28,6	6,5	4,0		3,0			0,0020	0,31
g	605262	2,7	27,6	6,9	3,9	1,0	1,0			0,0019	0,36
h	605263	1,0	28,7	6,6	4,0	1,0	1,0			0,0020	0,40

(continued)

	Heat	Mn	Cr	Ni	Mo	W	Co	Cu	Ru	B	N
in	605253	1,0	28,8	7,0	4,16		1,5			0,0019	0,37
j	605266	1,1	30,0	7,1	4,02					0,0018	0,38
k	605269	1,0	28,5	7,0	3,97	1,0	1,0			0,0020	0,45
l	605268	1,1	28,2	6,6	4,0	1,0	1,0	1,0		0,0021	0,43
m	605270	1,0	28,8	7,0	4,2		1,5		0,1	0,0021	0,41
n	605267	1,1	29,3	6,5	4,23			1,5		0,0019	0,38

Table 8. Thermo-Calc

Variant	α-formula empirical	α T-C	PRE total	PRE α	PRE γ	T_{max} sigma	Tmax Cr_2N
1	46	50	50,2	47,8	50,5	1006	1123
2	52	50	49,1	48,4	49,8	1019	1084
3	45	50	50,2	47,9	52,6	1007	1097
4	46	50	49,2	46,5	49,8	986	1121
5	47	50	49,1	48,5	49,7	1028	1038
6	52	50	48,1	47,1	49,2	998	1086
7	44	50	49,2	46,6	52,0	985	1081
8	46	50	48,1	47,2	49,1	1008	1044
e	46	53	49,3	48,4	49,5	1010	1099
f	65	52	46,7	47,2	46,1	1008	1090
g	48	51	48,4	48,4	48,3	1039	979
h	50	53	50,0	48,4	51,7	1035	1087
i	52	50	49,1	48,4	49,8	1019	1084

[0045] Thermo-Calc-values according to Table 8 (T-C version N thermodynamic database for steel TCFE99) are based on characteristic amounts for all specified elements in the different variations. The PRE-number for the ferrite and austenite is based on their equilibrium composition at 1100°C. T_{max} sigma is the dissolving temperature for the sigma phase, where high dissolving temperatures indicate lower structural stability.

[0046] The distribution of the alloying elements in the ferrite- and austenite phase was examined with microprobe analysis, the results appear from Table 9.

Table 9.

Heat	Phase	Cr	Mn	Ni	Mo	W	Co	Cu	N
605258	Ferrite	29,8	1,3	4,8	5,0		1,4		0,11
	Austenite	28,3	1,4	7,3	3,4		1,5		0,60
605249	Ferrite	29,8	1,1	5,4	5,1		1,3		0,10
	Austenite	27,3	1,2	7,9	3,3		1,6		0,53
605259	Ferrite	29,7	1,3	5,3	5,3		0,5		0,10
	Austenite	28,1	1,4	7,8	3,3		0,58		0,59
605260	Ferrite	28,4	1,3	4,4	5,0		1,4		0,08
	Austenite	26,5	1,4	6,3	3,6		1,5		0,54

(continued)

Heat	Phase	Cr	Mn	Ni	Mo	W	Co	Cu	N
605250	Ferrite	30,1	1,3	5,6	5,1		0,46		0,07
	Austenite	27,3	1,4	8,8	3,4		0,53		0,52
605251	Ferrite	29,6	1,2	5,0	5,2		1,3		0,08
	Austenite	26,9	1,3	7,6	3,5		1,5		0,53
605261	Ferrite	28,0	1,2	4,5	4,9		0,45		0,07
	Austenite	26,5	1,4	6,9	3,3		0,56		0,56
605252	Ferrite	29,6	1,3	5,3	5,2		0,42		0,09
	Austenite	27,1	1,4	8,2	3,3		0,51		0,48
605254	Ferrite	28,1	1,3	4,9	5,8		0,89		0,08
	Austenite	26,0	1,4	7,6	3,8		1,0		0,48
605255	Ferrite	30,1	1,3	5,0	4,7		2,7		0,08
	Austenite	27,0	1,3	7,7	3,0		3,3		0,45
605262	Ferrite	28,8	3,0	5,3	4,8	1,4	0,9		0,08
	Austenite	26,3	3,2	8,1	3,0	0,85	1,1		0,46
605263	Ferrite	29,7	1,3	5,1	5,1	1,3	0,91		0,07
	Austenite	27,8	1,4	7,7	3,2	0,79	1,1		0,51
605253	Ferrite	30,2	1,3	5,4	5,0		1,3		0,09
	Austenite	27,5	1,4	8,4	3,1		1,5		0,48
605266	Ferrite	31,0	1,4	5,7	4,8				0,09
	Austenite	29,0	1,5	8,4	3,1				0,52
605269	Ferrite	28,7	1,3	5,2	5,1	1,4	0,9		0,11
	Austenite	26,6	1,4	7,8	3,2	0,87	1,1		0,52
605268	Ferrite	29,1	1,3	5,0	4,7	1,3	0,91	0,84	0,12
	Austenite	26,7	1,4	7,5	3,2	0,97	1,0	1,2	0,51
605270	Ferrite	30,2	1,2	5,3	5,0		1,3		0,11
	Austenite	27,7	1,3	8,0	3,2		1,4		0,47
605267	Ferrite	30,1	1,3	5,1	4,9			1,3	0,08
	Austenite	27,8	1,4	7,6	3,1			1,8	0,46

[0047] The pitting corrosion properties of all heats have been tested in the "Green Death"- solution (1%$FeCl_3$, 1%$CuCl_2$, 11 % H_2SO_4, 1,2% HCl) for ranking. The test procedures are the same as pitting corrosion testing according to ASTM G48C, but the testing will be executed in a more aggressive solution than 6%$FeCl_3$, the so-called "Green Death"-solution. Also the general corrosion testing in 2%HCl (2 tests per heat) was executed for ranking before the dewpoint testing. The results from all tests appear from Table 10, Figure 2 and Figure 3. All tested heats perform better than SAF2507 in "Green Death"-solution. All heats lie within the identified range of 0,9-1,15; preferably 0,9-1,05 applicable for the ratio PRE austenit/PRE ferrite at the same time as PRE in both austenite and ferrite is in excess of 44 and for most of the heats even considerable in excess of 44. Some of the heats attain even the limit of total PRE 50. It is very interesting to note that heat 605251, alloyed with 1,5 weight-% cobalt, performs almost equivalent with heat 605250, alloyed with 0,6 weight-% cobalt, in "Green Death"-solution in spite of the lower chromium content in heat 605251. It is particularly surprising and interesting because heat 605251 has a PRE-number of ca. 48, which is in excess of some of today's commercial superduplex alloys simultaneously as the T_{max} sigma-value below 1010°C indicates a good structural stability based on the values in Table 2 in Example 1.

In Table 10 even PREW-number (%Cr+3,3%(Mo+0,5%W)+16%N) for the total composition of the alloy and PRE in austenite as well as in the ferrite (rounded off) based on composition of the phases are specified as measured with micro probe. Content of ferrite was measured after heat-treating at 1100°C followed by water quenching.

Table 10

Heat	α-halt	PREW Total	PRE α	PRE γ	PREγ/ PREα	CPT °C Green death
605258	48,2	50,3	48,1	49,1	1,021	
605249	59,8	48,9	48,3	46,6	0,967	75/80
605259	49,2	50,2	48,8	48,4	0,991	
605260	53,4	48,5	46,1	47,0	1,019	
605250	53,6	49,2	48,1	46,8	0,974	**95/80**
605251	54,2	48,2	48,1	46,9	0,976	**90/80**
605261	50,8	48,6	45,2	46,3	1,024	
605252	56,6	48,2	48,2	45,6	0,946	80/75
605254	53,2	48,8	48,5	46,2	0,953	90/75
605255	57,4	46,9	46,9	44,1	0,940	**90/80**
605262	57,2	47,9	48,3	45,0	0,931	
605263	53,6	49,7	49,8	47,8	0,959	
605253	52,6	48,4	48,2	45,4	0,942	85/75
605266	62,6	49,4	48,3	47,6	0,986	
605269	52,8	50,5	49,6	46,9	0,945	
605268	52,0	49,9	48,7	47,0	0,965	
605270	57,0	49,2	48,5	45,7	0,944	
605267	59,8	49,3	47,6	45,4	0,953	

[0048] In order to examine the structural stability in detail the samples were annealed for 20 minutes at 1080°C, 1100°C and 1150°C, whereafter they were quenched in water. The temperature, where the amount of intermetallic phase became insignificant was determined with help of investigations in a lightoptical microscope. A comparison of the structure of the heats after annealing at 1080°C followed by water quenching indicates which of the heats are more suspect to contain undesired sigma phase. The results are shown in Table 11. Control of the structure shows that the heats 605249, 605251, 605252, 605253, 605254, 605255, 605259, 605260, 605266 as well as 605267 are free from unwanted sigma phase. Moreover, heat 605249, alloyed with 1,5 weight-% cobalt, is free from sigma phase, while heat 605250, alloyed with 0,6 weight-% cobalt, contains a very small amount of sigma phase. Both heats are alloyed with high contents of chromium, approximately 29,0 weight-% and the molybdenum content of approximately 4,25 weight-%. If one compares the compositions of the heats 605249, 605250, 605251 and 605252 with thought on the content of sigma phase, it is very distinct that the range of composition for that optimum material is very narrow, in this case with regard to the structural stability. It further shows that the heat 605268 contains only sigma phase compared to heat 605263, which contains much sigma phase. What mainly distinguishes these heats from each other is the addition of copper to heat 605268. Heat 605266 and also 605267 are free from sigma phase, despite of a high content of chromium the later heat is alloyed with copper. Further, the heats 605262 and 605263 with addition of 1,0 weight-% tungsten show a structure with much sigma phase, while it is interesting to note that heat 605269, also with 1,0 weight-% tungsten but with higher content of nitrogen than 605262 and 605263 shows a considerable smaller amount of sigma phase. Consequently, a very well-leveled balance between the different alloying elements at these high alloying contents is required of for example chromium and molybdenum in order to obtain good structural properties.

Table 11 shows the results from the light optical examination after annealing at 1080°C, 20min followed by water quenching. The amount of sigma phase is specified with values from 1 to 5, where 1 represents that no sigma phase was detected in the examination, while 5 represents that a very high content of sigma phase was detected in the examination.

Table 11.

Heat	Sigma phase	Cr	Mo	W	Co	Cu	N	Ru
605249	1	28,8	4,23		1,5		0,38	
605250	2	28,8	4,24		0,6		0,40	
605251	1	28,1	4,24		1,5		0,38	
605252	1	28,4	4,23		0,5		0,37	
605253	1	28,8	4,16		1,5		0,37	
605254	1	26,9	4,80		1,0		0,38	
605255	1	28,6	4,04		3,0		0,31	
605258	2	29,0	4,23		1,5		0,46	
605259	1	29,0	4,23		0,6		0,45	
605260	1	27,5	4,22		1,5		0,44	
605261	2	27,8	4,22		0,6		0,43	
605262	4	27,6	3,93	1,0	1,0		0,36	
605263	5	28,7	3,96	1,0	1,0		0,40	
605266	1	30,0	4,02				0,38	
605267	1	29,3	4,23			1,5	0,38	
605268	2	28,2	3,98	1,0	1,0	1,0	0,43	
605269	3	28,5	3,97	1,0	1,0		0,45	
605270	3	28,8	4,19		1,5		0,41	0,1

[0049] In Table 12 the results from the impact strength testing of some of the heats are shown. The results are very good, which indicates a good structure after annealing at 1100°C followed by water quenching and the requirement of 100J will be managed with large margin of all tested heats.

Table 12.

Heat	Annealing [°C/min]	Quenching	Impact strength [J]	Impact strength [J]	Impact strength [J]
605249	1100/20	Water	>300	>300	>300
605250	1100/20	Water	>300	>300	>300
605251	1100/20	Water	>300	>300	>300
605252	1100/20	Water	>300	>300	>300
605253	1100/20	Water	258	267	257
605254	1100/20	Water	>300	>300	>300
605255	1100/20	Water	>300	>300	>300

[0050] Figure 4 shows the results from the hot ductility testing of the most of the heats. A good workability is of course of vital importance in order to be able to produce the material to product forms such as bars, tubes, such as welded and seamless tubes, plate, strip, wire, welding wire, constructive elements, such as for example pumps, valves, flanges and couplings. The heats 605249,605250, 605251, 605252, 605255, 605266 as well as 605267, the most with nitrogen content around 0,38 weight-% show somewhat improved hot ductility values.

Summary of the test results

[0051] In order to obtain good corrosion properties, simultaneously as the material shows good structural stability, hotworkability and weldability the material should be optimized according to the following:

- ☐ PRE-number in ferrite should exceed 45, but preferably be at least 47.
- ☐ PRE-number in austenit should exceed 45, but preferably be at least 47.
- ☐ PRE-number for the entire alloy should preferably be at least 46.
- ☐ Relationship PRE austenit/PRE ferrite should lie in the range of 0,9-1,15; preferably in the range 0,9-1,05.
- ☐ The content of ferrite should lie in the range preferably 45-55 volume-%.
- ☐ T_{max} sigma should not exceed 1010°C.
- ☐ The content of nitrogen should lie in the range 0,28-0,5 weight-%, preferably in the range 0,35-0,48 weight-%, but preferably 0,38-0,40 weight-%.
- ☐ The content of cobalt should lie in the range 0-3,5 weight-%, preferably 1,0-2,0 weight-%, but preferably 1,3-1,7 weight-%.
- ☐ In order to ensure the high nitrogen solubility, i.e. if the content of nitrogen is in the range 0,38-0,40 weight-% should at least 29 weight-% Cr be added as well as at least 3,0 weight-% Mo, thus the total content of the elements Cr, Mo and N fulfills said requirements on the PRE-number.

Claims

1. Ferritic-austenitic duplex stainless steel alloy, **characterized in, that** it shows the following composition, in weight-%:

C	max 0,03%
Si	max 0,5%
Mn	0 - 3,0%
Cr	24,0 - 30,0%
Ni	4,9 - 10,0%
Mo	3,0 - 5,0%
N	0,28 - 0,5%
B	0 - 0,0030%
S	max 0,010%
W	0 - 3,0%
Cu	0 - 2,0%
Ru	0 - 0,3%
Al	0 - 0,03%
Ca	0 - 0,010%
Ti	0 - 0,35 %
V	0 - 0,55 %

balance Fe and normal occurring impurities, whereby the content of ferrite is 40-65 volume-%.

2. Alloy according to claim 1, **characterized in, that** the content of manganese lies between 0,5 and 1,2 weight-%.

3. Alloy according to claim 1 or 2, **characterized in, that** the content of chromium lies between 27,0 and 29,0 weight-%.

4. Alloy according to claim 1-3, **characterized in, that** the content of nickel lies between 5,0 and 8,0 weight-%.

5. Alloy according to claim 1-4, **characterized in, that** the content of molybdenum lies between 3,6 and 4,7 weight-%.

6. Alloy according to claim 1-5, **characterized in, that** the content of nitrogen lies between 0,35 and 0,45 weight-%.

7. Alloy according to claim 1-5, **characterized in, that** the content of ruthenium is higher than 0 and up to 0,1 weight-%.

8. Alloy according to any of preceding claims, **characterized in, that** the content of copper lies between 0,5 and 2,0 weight-%, preferably between 1,0 and 1,5 weight-%.

9. Alloy according to any of preceding claims, **characterized in, that** the content of ferrite lies between 42 and 60 volume-%, preferably between 45 and 55 volume-%.

10. Alloy according to any of preceding claims, **characterized in, that** the total PRE- or PREW-value of the alloy exceeds 44, whereby PRE = %Cr + 3,3%Mo + 16N and PREW = %Cr + 3,3(%Mo + 0,5%W) + 16N, wherein % considers weight-%.

11. Alloy according to any of preceding claims, **characterized in, that** the PRE- or PREW-value for both ferrite- and austenite phase is higher than 45 and PRE or PREW-value for the total composition of the alloy is higher than 46.

12. Alloy according to claim 10 or 11, **characterized in, that** the PRE- or PREW-value for both ferrite- and austenite phase lies between 47 and 49.

13. Alloy according to claim 10, 11 or 12, **characterized in, that** the ratio between PRE(W)-value for austenite phase and PRE(W)-value for the ferrite phase lies between 0,90 and 1,15; preferably between 0,9 and 1,05.

14. Alloy according to any of preceding claims for use in chloride-containing environments.

15. Alloy according to any of preceding claims for use in chloride-containing environments in product forms such as bars, tubes, such as welded and seamless tubes, plate, strip, wire, welding wire, constructive parts, such as for example pumps, valves, flanges and couplings.

Figure 1

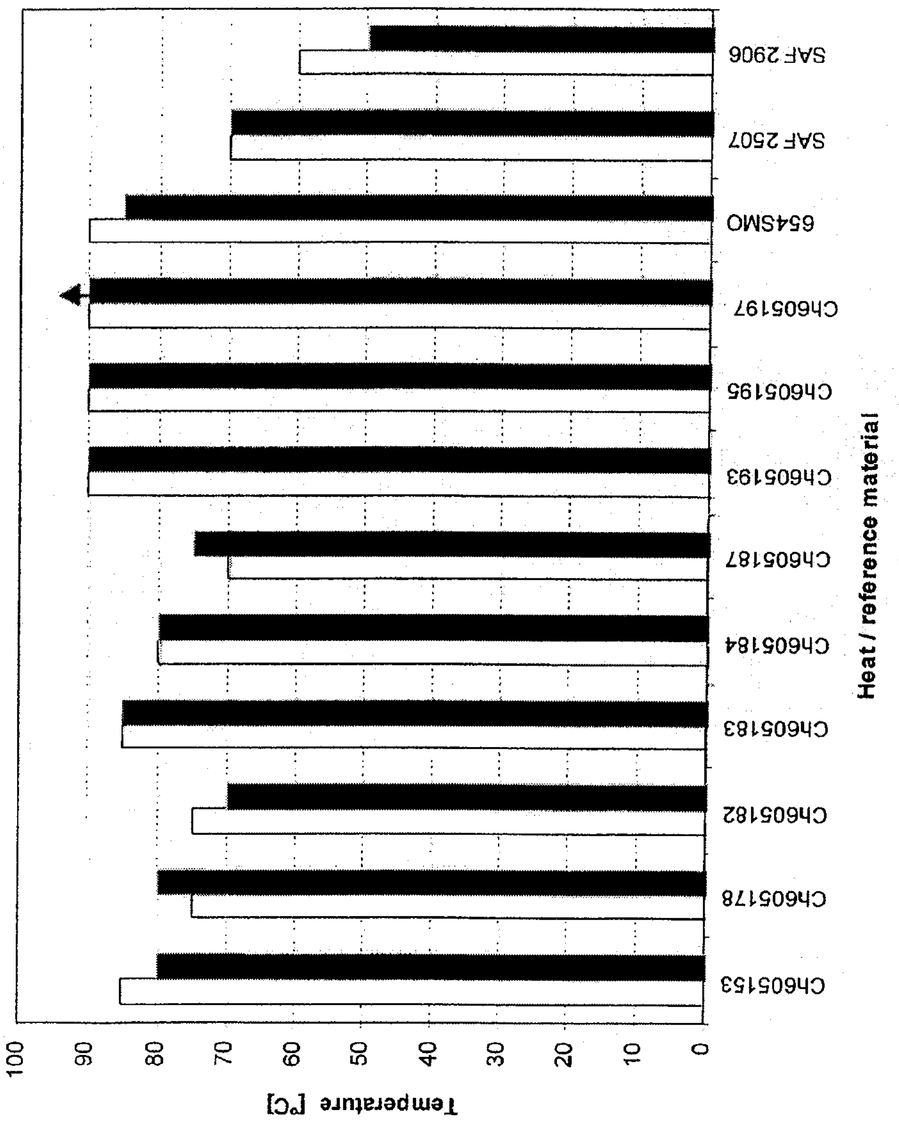

Temperature [°C]
0
10
20
30
40
50
60
70
80
90
100
Heat / reference material
Ch605153
Ch605178
Ch605182
Ch605183
Ch605184
Ch605187
Ch605193
Ch605195
Ch605197
654SMO
SAF 2507
SAF 2906

Figure 2

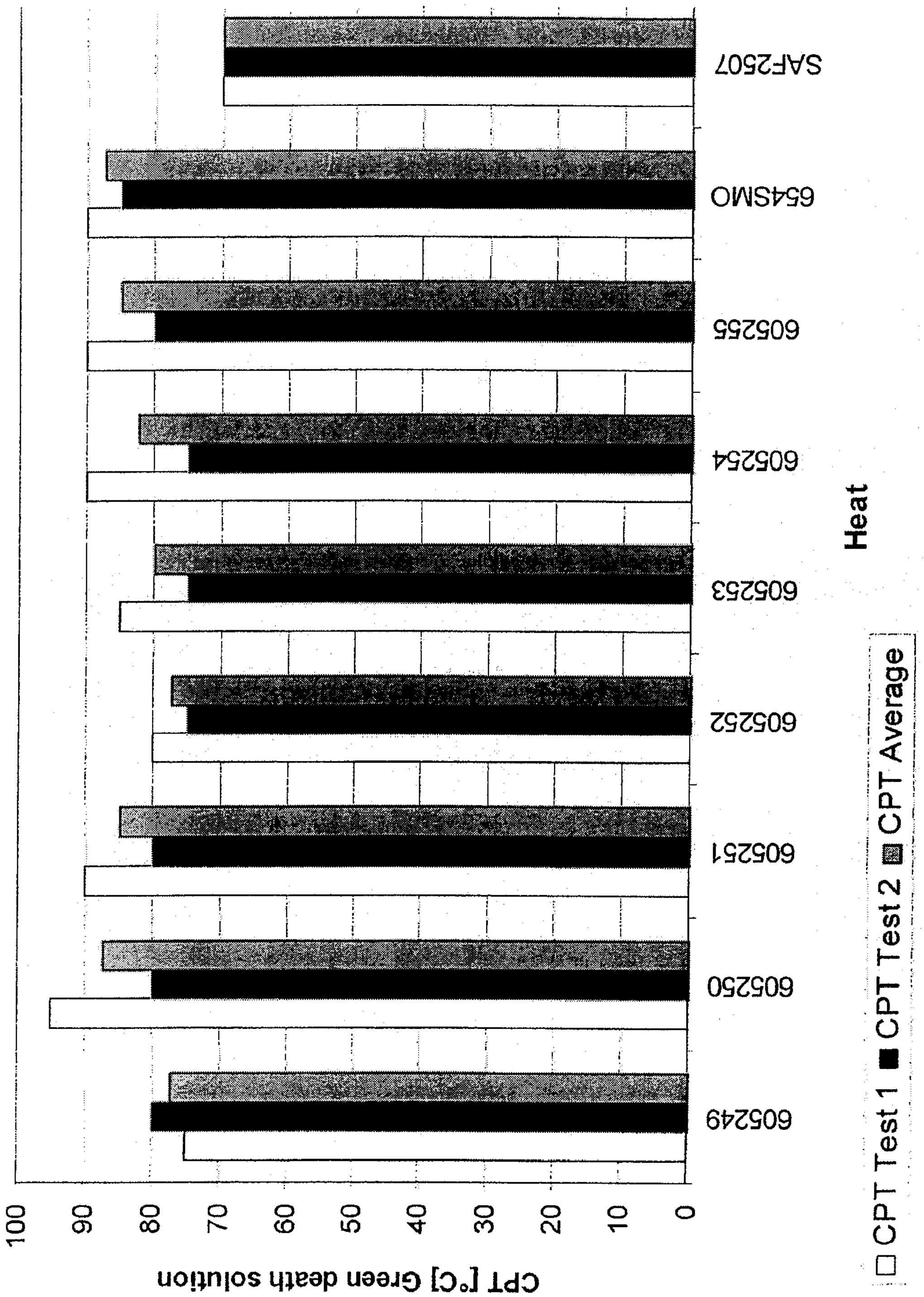

CPT [°C] Green death solution
0
10
20
30
40
50
60
70
80
90
100
605249
605250
605251
605252
605253
605254
605255
654SMO
SAF2507
Heat
□ CPT Test 1 ■ CPT Test 2 ▨ CPT Average

Figure 3

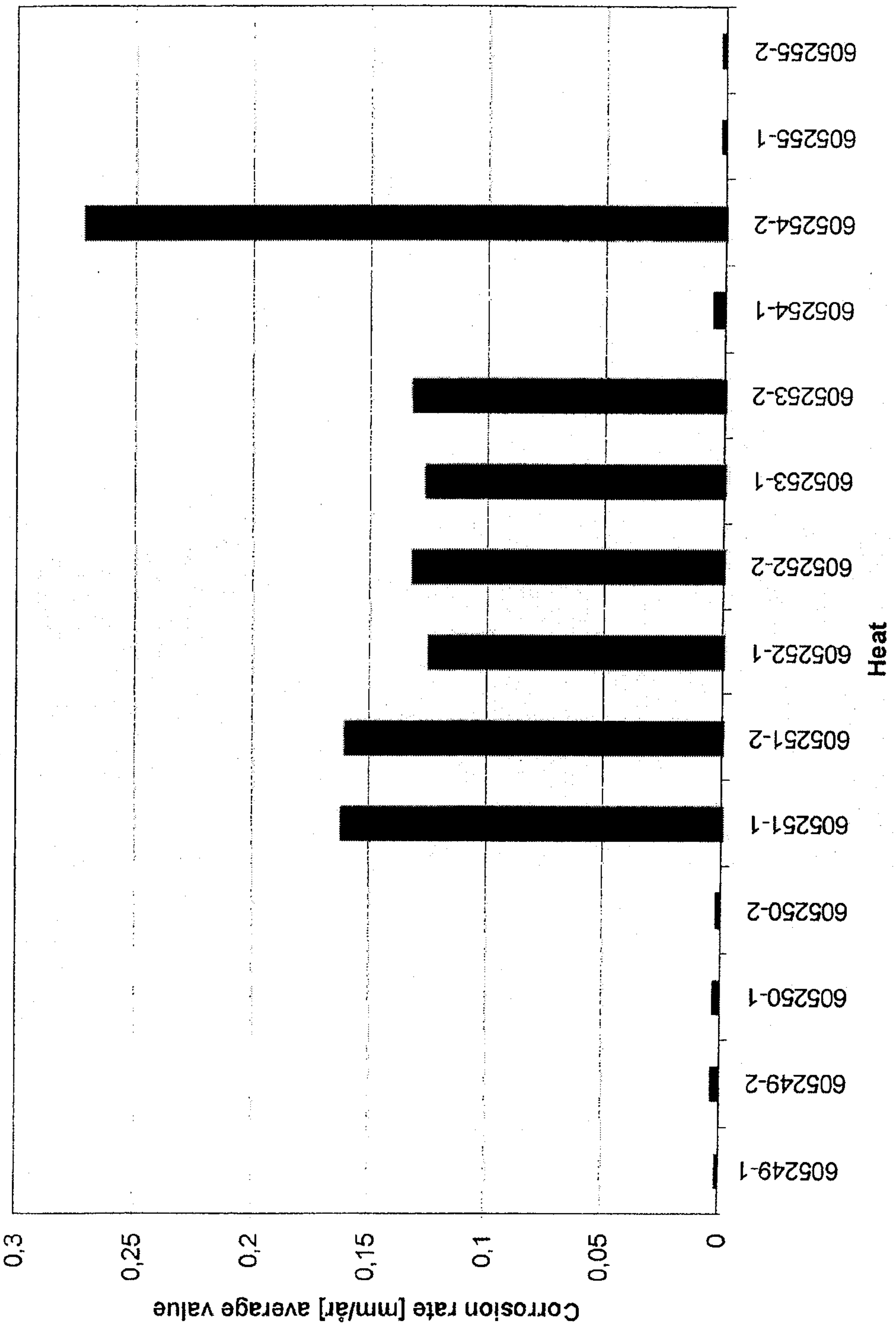
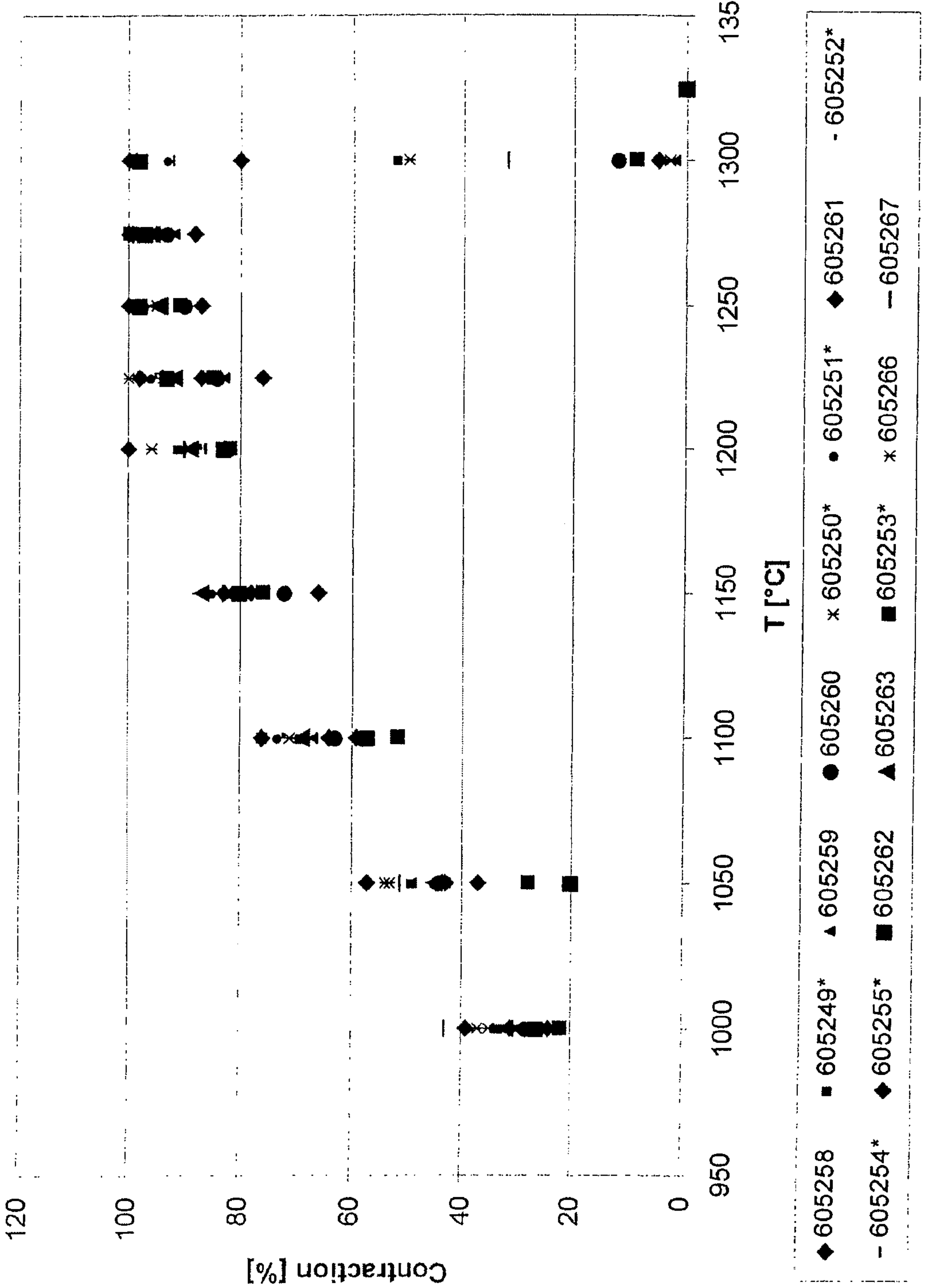

Corrosion rate [mm/år] average value
0
0,05
0,1
0,15
0,2
0,25
0,3
Heat
605249-1
605249-2
605250-1
605250-2
605251-1
605251-2
605252-1
605252-2
605253-1
605253-2
605254-1
605254-2
605255-1
605255-2

Figure 4


Contraction [%]
120
100
80
60
40
20
0
T [°C]
950
1000
1050
1100
1150
1200
1250
1300
1350
◆ 605258
▪ 605249*
▴ 605259
● 605260
⁎ 605250*
• 605251*
◆ 605261
- 605252*
- 605254*
◆ 605255*
■ 605262
▲ 605263
■ 605253*
⁎ 605266
— 605267

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 06 11 3879

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	EP 0 220 141 A (SANTRADE LTD) 29 April 1987 (1987-04-29) * page 1 - page 2 * * page 11; example 3 * * page 13; example 4 * -----	1-10,14, 15	INV. C22C38/44
X	EP 0 534 864 A (SUMITOMO METAL INDUSTRIES, LTD) 31 March 1993 (1993-03-31) * abstract * * page 2, lines 1-6 * * page 3, lines 3-23 * * page 5, lines 45-58 * * examples 2,3; table 1 * -----	1-10,14, 15	
X	EP 0 545 753 A (SUMITOMO METAL INDUSTRIES, LTD) 9 June 1993 (1993-06-09) * abstract * * page 2, lines 1-20 * * page 3, lines 1-17 * * tables 1,2 * -----	1-9,14, 15	
X	US 4 765 953 A (HAGENFELDT ET AL) 23 August 1988 (1988-08-23) * the whole document * -----	1-9,14, 15	TECHNICAL FIELDS SEARCHED (IPC) C22C
X	SE 514 816 C2 (SANDVIK AB) 30 April 2001 (2001-04-30) * page 1, lines 4-7 * * page 4, lines 23-32 - page 5 * * page 6, lines 16-21 *	1-7,9, 10,14,15	
X,P	& US 2001/031217 A1 (BERGSTROM ORJAN ET AL) 18 October 2001 (2001-10-18) * paragraphs [0001], [0022] - [0024] * * table 1 * * table 5 * -----	1-7,9, 10,14,15	
A,P	EP 1 129 230 A (SANDVIK AKTIEBOLAG) 5 September 2001 (2001-09-05) * the whole document * -----	1-15	

The present search report has been drawn up for all claims

1

Place of search	Date of completion of the search	Examiner
Munich	21 June 2006	Brown, A

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons
....
& : member of the same patent family, corresponding document

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 06 11 3879

21-06-2006

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0220141 A	29-04-1987	AU 586024 B2	29-06-1989
		AU 6230486 A	12-03-1987
		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
		JP 2107118 C	06-11-1996
		JP 8026435 B	13-03-1996
		JP 62056556 A	12-03-1987
		KR 9309984 B1	13-10-1993
		NO 863541 A	06-03-1987
		SE 453838 B	07-03-1988
		SE 8504131 A	06-03-1987
		US 4765953 A	23-08-1988
		ZA 8606550 A	29-04-1987
EP 0534864 A	31-03-1993	JP 3227734 B2	12-11-2001
		JP 5093246 A	16-04-1993
		US 5284530 A	08-02-1994
EP 0545753 A	09-06-1993	AT 133716 T	15-02-1996
		AU 650799 B2	30-06-1994
		AU 2830392 A	13-05-1993
		DE 69208059 D1	14-03-1996
		DE 69208059 T2	11-07-1996
		ES 2089456 T3	01-10-1996
		JP 2500162 B2	29-05-1996
		JP 5132741 A	28-05-1993
		US 5298093 A	29-03-1994
US 4765953 A	23-08-1988	AU 586024 B2	29-06-1989
		AU 6230486 A	12-03-1987
		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 2107118 C	06-11-1996
		JP 8026435 B	13-03-1996
		JP 62056556 A	12-03-1987
		KR 9309984 B1	13-10-1993
		NO 863541 A	06-03-1987
		SE 453838 B	07-03-1988
		SE 8504131 A	06-03-1987

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 06 11 3879

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

21-06-2006

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 4765953 A		ZA 8606550 A	29-04-1987
SE 514816 C2	30-04-2001	AU 4132001 A	12-09-2001
		CA 2397592 A1	07-09-2001
		EP 1259656 A1	27-11-2002
		JP 2003525354 T	26-08-2003
		NO 20024150 A	30-10-2002
		SE 0000678 A	30-04-2001
		WO 0164969 A1	07-09-2001
		US 2001031217 A1	18-10-2001
US 2001031217 A1	18-10-2001	AU 4132001 A	12-09-2001
		CA 2397592 A1	07-09-2001
		EP 1259656 A1	27-11-2002
		JP 2003525354 T	26-08-2003
		NO 20024150 A	30-10-2002
		SE 514816 C2	30-04-2001
		SE 0000678 A	30-04-2001
		WO 0164969 A1	07-09-2001
EP 1129230 A	05-09-2001	AT 250151 T	15-10-2003
		DE 69911452 D1	23-10-2003
		DE 69911452 T2	22-07-2004
		ES 2205910 T3	01-05-2004
		JP 2002529599 T	10-09-2002
		SE 514044 C2	18-12-2000
		SE 9803633 A	24-04-2000
		WO 0028101 A1	18-05-2000
		US 6451133 B1	17-09-2002

REFERENCES CITED IN THE DESCRIPTION

Patent documents cited in the description

- EP 0220141 A **[0002]**
- EP 0545753 A **[0004]**
- EP 0708845 A **[0005]**
- US 4985091 A **[0006]**
- US 6048413 A **[0007]**