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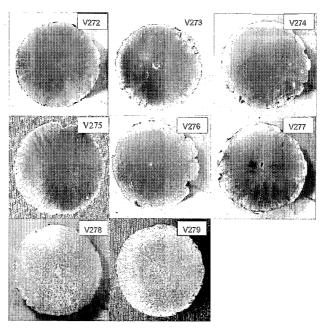
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(54) Title: AN AUSTENITIC STEEL AND A STEEL PRODUCT



(57) Abstract: High-alloy austenitic stainless steels that are extra resistant to pitting and crevice corrosion in aggressive, chloridecontaining solutions have a tendency for macro-segregation of Mo, at solidification of the melt. This problem is solved by an super austenite stainless steel having the following composition, in % by weight: max 0.03 C max 0.5 Si max 6 Mn 28-30 Cr 21-24 Ni 4-6 % (Mo + W/2), the content of W being max 0.7 0.5-1.1 N max 1.0 Cu balance iron and impurities at normal contents originating from the production of the steel.

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An austenitic steel and a steel product.

TECHNICAL FIELD

The present invention relates to an austenitic stainless steel with good strength, good impact strength, good weldability and good corrosion resistance, in particular a good resistance against pitting and crevice corrosion. The invention also relates to a product manufactured from the austenitic stainless steel.

10 PRIOR ART

When the stainless, austenitic steel Avesta 254 SMO[®], containing a little more than 6 % molybdenum, (Mo), (US-A-4 078 920) was introduced on the market, more than twenty years ago, a significant technical progress was achieved, since corrosion and strength properties were considerably much better than for high-alloy steels existing then.

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- In the present text, the terms "content" and "percentage" always refer to the content in "% by weight", and in case only a numerical value is given, it refers to content in % by weight.
- The sensitivity to pitting is an Achilles' heel to stainless steels. It is well known that the elements chromium (Cr), Mo and nitrogen(N) prevent pitting, and a great number of steels exist that are well protected against this type of corrosion. Such steels are also improved in terms of crevice corrosion resistance, which is similarly affected by the same elements. The superaustenitic steels are in a class of their own. The
- superaustenitic steels are usually defined as steels having a pitting resistance equivalent PRE > 40. PRE is often defined as % Cr + 3.3 % Mo + 30 % N. A great number of super austenite steels have been described during the past thirty years, but only a limited number are of commercial significance. Of those steels can be mentioned the above mentioned 254 SMO (EN 1.4547, UNS S31254), 19-25hMo (EN 1.4529, UNS N08926)
- and AL-6XN (UNS N08367) (US-A-4 545 826, McCunn et al.). These superaustenitic steels are of 6Mo-steel type, having about 20 % Cr, 6 % Mo and 0.20 % N, which gives a PRE > 46, and they have been used with great success since the 1980's.
- The large effect by N on pitting makes it interesting to add higher contents than about 0.2 %. Traditionally, high contents of manganese have been used in order to dissolve high contents of N in the steel. One example of such a steel is 4565 (EN 1.4565, UNS S34565), having 24 % Cr, 6 % Mn, 4.5 % Mo and 0.4 % N and a PRE-level similar to

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that of the 6Mo-steels according to the above (DE-C1-37 29 577, Thyssen Edelstahlwerke).

An increased content of Mo is of course valuable in order to further increase pitting resistance. This has been done in the steel Avesta 654 SMO[®], (EN UNS S 32654) having 24% Cr, 3.5% Mn, 7.3% Mo, 0.5% N (US-A-5 141 705). This steel has a PRE-level as high as > 60, and in many respects it is equally corrosion resistant as the best nickel alloys. By the high Cr and Mo contents, as much as 0.5 % N could be dissolved at a fairly moderate Mn content. The high N content gives the steel a good strength combined with a good ductility. A quite similar variant of 654 SMO, in which a certain part of the Mo is exchanged for W, is the steel B66 (EN 1.4659, UNS S 31266) (US-A-5 494 636, Dupoiron et al.).

One problem of fully austenitic steels with high contents of Mo is the severe segregation tendency of Mo. This results in segregated areas in ingots or continuous casts, still largely remaining in the final products and giving rise to precipitations of intermetallic phases, such as a sigma phase. This phenomenon is particularly prominent in the most highly alloyed steels, and various procedures exist in order to counteract or reduce the effects thereof in latter stages.

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In continuous casting of steels with a tendency for segregations, there is a risk of macrosegregations leading to various problems in the final product. Macro-segregations form by alloying elements being distributed between the solid phase and residual melt, during the casting, such that differences in composition arise between different areas of the solidified blank, depending on cooling, flows and manner of solidification. So called Aand V-segregations are classical for ingots, as well as centre segregations in continuous casting. It is well established that Mo is an element having a particularly high tendency for segregation, and hence, steels of the highest Mo contents often exhibit severe macrosegregations. Such macro-segregations are difficult to eliminate in subsequent production steps, and most often result in precipitation of intermetallic phases. Such phases can cause laminations in rolling, and also impair product properties such as corrosion resistance and toughness. Hence, superaustenitic steels with a very high content of Mo often get centre segregations in continuously cast blanks, which severely limit the possibility to produce homogeneous sheets of optimum properties. The problems are particularly pronounced in sheets with greater thicknesses and sheets with a thickness greater than 15 mm is hardly produced without deterioration of the properties. Hence, a need exists for a high-alloy austenitic stainless steel that is not

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prone to macro-segregations and which can be used in the manufacturing of products of greater thickness.

BRIEF ACCOUNT OF THE INVENTION

The object of the present invention is accordingly to achieve a new austenitic stainless steel that is highly alloyed, especially in terms of Cr, Mo and N. The so called superaustenitic steel is characterised by very good corrosion resistance and strength. The steel is adapted, in various processed forms, such as sheets, bars and pipes, for use in aggressive environments in chemical industry, power plants and various seawater applications.

The invention aims especially at achieving a material that advantageously can be used within the following fields of application:

- 15 within off-shore industry (seawater, acidic oil and gas)
 - for heat exchangers and condensers (seawater)
 - for desalination plants (saltwater)
 - for equipment for flue gas cleaning (chloride acids)
 - for equipment for flue gas condensing (strong acids)
- 20 in sulphuric and phosphoric acid works (strong acids)
 - for pipes and equipment for generation of oil and gas (acidic oil and gas)
 - for equipment and pipes in cellulose bleaching plants and in chlorate works
 (chloride, oxidizing acids and solutions, respectively)
 - for tankers and tank lorries (all types of chemicals)

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This object is achieved by an austenitic stainless steel having the following composition, in % by weight:

max 0.03 C

max 0.5 Si

30 max 6 Mn

28-30 Cr

21-24 Ni

4-6% (Mo + W/2), the content of W being max 0.7

0.5-1.1 N

35 max 1.0 Cu

balance iron and impurities at normal contents originating from the production of the steel.

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It has been shown that by limiting the content of Mo, and alloying-in more CR, a superaustenitic steel is achieved having a very good pitting resistance and markedly lower tendency for structural segregations.

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Besides the mentioned alloying elements, the steel may also contain small contents of other elements, provided that these will not negatively affect the desired properties of the steel, which properties are mentioned above. The steel may e.g. contain boron at a content of up to 0.005 % B, with the purpose of achieving an additional increase of the steel's ductility in hot working. In case the steel contains cerium, the steel normally also contains other rare earth metals, since such elements, including cerium, are normally added in the form of a mish-metal at a content of up to 0.1 %. Calcium and magnesium can furthermore also be added to the steel at contents of up to 0.01 %, and aluminium can be added to the steel at contents of up to 0.05 %, of the respective elements, for different purposes.

Considering the various alloying materials, the following furthermore applies:

In this steel, carbon is to be seen mainly as a non-desired element, since carbon will severely lower the solubility of N in the melt. Carbon also increases the tendency for precipitation of harmful Cr carbides, and for these reasons it should not be present at contents above 0.03 %, and preferably it should be 0.015-0.025 %, suitably 0.020 %.

Silicon increases the tendency for precipitation of intermetallic phases, and severely lowers the solubility of N in the steel melt. Therefore, silicon should exist at a content of max 0.5 %, preferably max 0.3 %, suitably max 0.25 %.

Manganese is added to the steel in order to affect the solubility of N in the steel, as is known per se. Therefore, manganese is added to the steel at a content of up to 6 %, preferably at least 4.0 % and suitably 4.5-5.5 %, most preferred about 5.0 %, in order to increase the solubility of N in the molten phase. High contents of manganese will however lead to problems in decarburization, since the element, just as Cr, will lower the activity of carbon, whereby decarburization becomes slower. Manganese has moreover a high steam-pressure and a high affinity for oxygen, which means that if the content of manganese is high, a considerable amount of manganese will be lost in decarburization. It is also known that manganese can form sulphides that will lower the resistance against pitting and crevice corrosion. Research in connection with the

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development of the inventive steel has also shown that manganese dissolved in the austenitic will impair corrosion resistance also when manganese sulphides are non-present. For these reasons, the content of manganese is limited to max 6 %, preferably max 5.5 %, suitably about 5.0 %.

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Cr is a particularly important element in this, as in all, stainless steels. Cr will generally increase corrosion resistance. It also increases the solubility of N in molten phase more strongly than other elements of the steel. Therefore, Cr should exist in the steel at a content of at least 28.0 %.

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However, Cr, especially in combination with Mo and silicon, will increase the tendency of precipitation of intermetallic phases, and in combination with N, it also increases the tendency for precipitation of nitrides. This will influence for example welding and heat treatment. For this reason, the content of Cr is limited to 30%, preferably max 29.0 %, suitably to 28.5%.

Nickel is an austenitic former, and is added in order to, in combination with other austenitic formers, give the steel its austenitic micro-structure. An increased content of nickel will also counteract precipitation of intermetallic phases. For these reasons, nickel should exist in the steel at a content of at least 21 %, preferably at least 22.0 %.

Nickel will however lower the solubility of N in the steel, in the molten phase, and will also increase the tendency for precipitation of carbides in the solid phase. Moreover, nickel is an expensive alloying element. Hence, the content of nickel is limited to max 24 %, preferably max 23 %, suitably max 22.6 % Ni.

Mo is one of the most important elements in this steel, by strongly increasing corrosion resistance, especially against pitting and crevice corrosion, at the same time as the element increases the solubility of N in the molten phase. The tendency for nitride precipitation also decreases at an increasing content of Mo. Therefore, the steel should contain more than 4 % Mo, preferably at least 5 % Mo. It is however well established that Mo is an element of particularly large tendency for segregation. The segregations are difficult to eliminate in subsequent production steps. Moreover, Mo will increase the tendency for precipitation of intermetallic phases, e.g. in welding and heat treatment.

For these reasons, the content of Mo must not exceed 6 %, and preferably it is about 5.5 %.

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If tungsten is included in the stainless steel, it will interact with Mo, such that the above given contents of Mo will be total contents of Mo + W/2, i.e. the actual contents of Mo will have to be lowered. The maximum content of tungsten is 0.7 % W, preferably max 0.5 %, suitably max 0.3 %, and even more preferred max 0.1 % W.

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Also N is an important alloying element of the present steel. N will increase resistance against pitting and crevice corrosion very strongly, and will radically increase strength, at the same time as a good impact strength and workability is maintained. N is at the same time a cheap alloying element, since it can be alloyed into the steel via a mixture of air and N gas, in the decarburization in a converter.

N is also a strongly austenitic stabilising alloying element, which also gives several advantages. Some alloying elements will segregate strongly in connection with welding. This is particularly true for Mo, that exists at high contents in the steel according to the invention. In the interdendritic areas, the contents of Mo will most often be so high that the risk of precipitation of intermetallic phases becomes high. During the research for the steel according to the invention, it has surprisingly been shown that austenitic stability is so good that the interdendritic areas, despite the high contents of Mo, will retain their austenitic microstructure. The good austenite stability is an advantage e.g. in connection with welding without additives, since it results in the weld deposit having extremely low contents of secondary phases, and thus a higher ductility and corrosion resistance.

The most common intermetallic phases in this type of steel are Laves' phase, sigma phase, and chi phase. All these phases have very low or none N solubility. For this reason, the N can delay precipitation of Laves' phase, sigma phase and chi phase. A higher content of N will accordingly increase stability against precipitation of intermetallic phases. For these reasons, N should exist in the steel at a content of at least 0.5%, preferably at least 0.6% N.

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Too high contents of N will however increase the tendency for precipitation of nitrides. High contents of N will also impair hot workability. Therefore, the N content of the steel should not exceed 1.1%, preferably max 0.9 %, and even more preferred max 0.8% N. A preferred amount of N lay in the interval of 0.6-0.8 % N.

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It is known that in certain austenitic stainless steels, copper can improve corrosion resistance against certain acids, while resistance against pitting and crevice corrosion

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can be impaired at too high contents of copper. Therefore, copper can exist at significant contents in the steel of up to 1.0 %. Extensive research has shown that there is an optimum content range for copper, concerning corrosion properties in various media. For this reason, copper should be added at a content of at least 0.5 %, but suitably within the range of 0.7-0.8 % Cu.

Cerium may optionally be added to the steel, e.g. in the form of a mish metal, in order to improve hot workability for the steel, as is known per se. In case a mish metal is added, the steel will besides cerium also contain other rare earth metals, such as Al, Ca and

- Mg. In the steel, cerium will form cerium oxy sulphides that do not impair corrosion resistance as much as other sulphides do, such as manganese sulphide. For these reasons, cerium and lanthanum may be included in the steel at significant contents of up to max 0.1 %.
- Preferably, the alloying elements of the stainless steel are balanced against each other such that the steel contains Cr, Mo and N at such an amount that a PRE-value of at least 60 is achieved, where PRE = Cr + 3.3Mo + 1.65W + 30N. Suitably, the PRE-value is at least 64, most preferred at least 66.
- In a particularly preferred embodiment, the austenitic stainless steel has a composition containing, in % by weight:

max 0.02 C

0.3 Si

5.0 Mn

25 28.3 Cr

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22.3 Ni

5.5 Mo

0.75 Cu

0.65 N

- balance iron and impurities at normal contents originating from the production of the steel, and after heat treatment at a temperature of 1150-1220 °C, the steel has a homogeneous microstructure mainly consisting of austenite and being essentially free from harmful amounts of secondary phases.
- Austenitic stainless steels having a composition according to the above are very well suited to be continuously cast to form flat or long products. Without any remelting process, they can be hot rolled to a final dimension of up to 50 mm at a reduction rate of

at least 1:3 with a low level of segregation. After heat treatment at a temperature of 1150-1220 °C they have a micro-structure mainly formed by austenite and essentially free from harmful amounts of secondary phases. Of course, the steel is also suited for other methods of manufacturing, such as ingot casting and powder metallurgical handling.

BRIEF DESCRIPTION OF THE ENCLOSED DRAWINGS

- Fig. 1 shows macro-photographs of various ingots, in cross-section.
- Fig. 2 shows micro-photographs of various cast alloys.
- Fig. 3 shows micro-photographs of some representative cast alloys after full annealing at 1180 °C for 30 min, and quenching in water.

UNDERTAKEN EXPERIMENTS

Laboratory ingots of 2.2 kg respectively were produced of high Cr alloys as well as commercial steels 654 SMO[®] and B66. A high frequency induction furnace with N or argon as protective gas was used for melting. Detailed melting data is summarized in Table 1. In the experiments, charges V274, V275, V278 and V279 are denoted 28Cr, and they are of compositions that in the main correspond to steels according to the present patent application. The dimensions of the laboratory ingots were a length of about 190 mm and a middle diameter of 40 mm. Samples were taken both in cross-section, for metallographic analysis, and longitudinally for pitting studies.

Table 1

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Alloys	Charge No.	Liquidus temperature (°C)*	Tapping temperature	Superheat temperature	Protective gas	Macro- crevices
			(°C)	ΔT(°C)		/pores
654 SMO	V272	1320	1668	348	400 torr N ₂	No
B66	V273	1332	1553	221	400 torr N ₂	Yes
28Cr	V274	1297	1420	123	200 torr Ar	Yes
28Cr	V275	1297	1445	148	200 torr Ar	No
654 SMO	V276	1320	1418	98	200 torr Ar	Yes
B66	V277	1331	1486	155	200-760	No
					torr Ar	
28Cr	V278	1297	1385	88	200-760	No
					torr N ₂	
28Cr	V279	1297	1387	90	200-760	No
			-		torr N ₂	

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METALLOGRAPHIC ANALYSIS

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The samples, from cast as well as annealed ingots, were face-ground, polished and etched. Björk's solution (5 g FeCl₃·6H₂O + 5 g CuCl₂ + 100 ml HCl + 150 ml H₂O + 25 ml C₂H₅OH) was used for macro-structural etching, and modified V2A (100 ml H₂O + 100 ml HCl + 5 ml HNO₃ + 6 g FeCl₃·6H₂O) was used for micro-structural etching.

The chemical compositions of all tested charges are given in Table 2, in which all numerical data in bold font deviate from the standard specification for the commercial steels. All analysed samples were taken from the bottom parts of the ingots. For charges V278 and V279, both the top part and the bottom part were analysed, showing a homogeneous chemical composition of the ingots. Alloy 28Cr has a high solubility of N, 0.72 % by weight of N being achieved in the steel. It seems possible to increase N content even further. The reason for this is believed to be that the increase of Cr and manganese contents has a truly positive effect on the solubility of N.

Table 2

Y Charge No. Original C Si Mn P S Cr Ni Mo SMO Original 0.014 0.24 3.37 0.020 0.000 24.25 21.84 7.27 SMO V272 0.012 0.46 3.19 0.021 0.002 24.57 22.11 7.29 SMO V275 0.013 0.25 3.51 0.015 0.002 24.80 22.40 7.27 SMO V276 0.013 0.25 3.51 0.015 0.002 23.38 21.64 5.33 Intert V273 0.014 0.20 0.002 22.38 21.64 5.33 Intert V277 0.014 0.020 0.021 20.01 22.91 22.40 7.27 Intert V277 0.017 0.22 0.021 0.004 22.13 5.56 Intert V278 0.017 0.22 0.015 0.022 22.18 22.15 5.56<	Chemical o	ompositions of v	various in	gots (% b	y weight	zabie z Bold font n	le z at numeri	cal data i	s outside s	tandard sn	ecification	ASTM 4	240
SMO Original 0.014 0.24 3.37 0.020 0.000 24.25 21.84 7.27 SMO V272 0.012 0.46 3.19 0.021 0.002 24.57 22.11 7.29 SMO V272 0.013 0.25 3.51 0.015 0.002 24.80 22.40 7.27 SMO V276 0.013 0.25 3.51 0.015 0.002 24.80 22.40 7.27 SMO V276 0.014 1.30 1.09 0.018 0.001 22.91 22.91 22.40 7.27 V274 0.014 0.20 0.22 0.021 0.004 28.48 22.41 5.59 r (top) V274 0.017 0.27 5.24 0.013 0.002 27.98 22.11 5.56 r (top) V278 0.017 0.27 5.32 0.015 0.002 28.47 22.16 5.58 com) V278 0.019 <t< td=""><td>VIIoy</td><td>Charge No.</td><td>С</td><td>Si</td><td>Mn</td><td>P</td><td>S</td><td>Cr</td><td>Ν̈</td><td>Mo</td><td>Ti</td><td>Nb</td><td>Ca</td></t<>	VIIoy	Charge No.	С	Si	Mn	P	S	Cr	Ν̈	Mo	Ti	Nb	Ca
SMO V2772 0.012 0.46 3.19 0.021 0.002 24.57 22.11 7.29 SMO V276 0.013 0.25 3.51 0.015 0.002 24.80 22.40 7.27 SMO Original 0.016 0.19 3.14 0.022 0.002 24.80 22.40 7.27 V273 0.014 1.30 1.09 0.018 0.001 22.91 22.08 5.65 V277 0.017 0.20 3.36 0.012 0.004 24.01 22.08 5.74 r V2774 0.019 0.26 5.24 0.013 0.002 27.84 22.11 5.59 r V2774 0.019 0.26 5.32 0.015 0.002 28.42 22.15 5.59 r V2778 0.017 0.27 5.32 0.015 0.002 28.42 22.15 5.56 r V278 0.019 0.27 5.32 0.015	554 SMO	Original sheet	0.014	0.24	3.37	0.020	0.000	24.25	21.84	7.27		0.00	0,49
SMO V276 0.013 0.25 3.51 0.015 0.002 24.80 22.40 7.27 sheet sheet 0.016 0.19 3.14 0.022 0.002 23.38 21.64 5.33 V273 0.014 1.30 1.09 0.018 0.001 22.91 22.08 5.65 V277 0.017 0.20 3.36 0.021 0.004 24.01 22.08 5.65 r V277 0.017 0.23 4.99 0.012 0.004 24.01 22.08 5.74 r V274 0.020 0.23 4.99 0.012 0.004 24.01 22.08 5.74 r V274 0.017 0.27 5.24 0.013 0.002 28.42 22.11 5.56 r V278 0.017 0.27 5.32 0.015 0.002 28.47 22.05 5.58 r V278 0.017 0.27 5.32 0.014	554 SMO	V272	0.012	0.46	3.19	0.021	0.002	24.57	22.11	7.29	<0.001	0.010	0.52
Sheet 0.014 0.19 3.14 0.022 0.002 23.38 21.64 5.33 sheet v273 0.014 1.30 1.09 0.018 0.001 22.91 22.08 5.65 r V277 0.017 0.20 3.36 0.021 0.004 24.01 22.08 5.74 r V2774 0.017 0.23 4.99 0.012 0.004 28.48 22.11 5.59 r V2774 0.019 0.26 5.24 0.013 0.002 27.98 22.11 5.59 r V2774 0.019 0.27 5.32 0.015 0.002 28.47 22.15 5.56 r V278 0.017 0.27 5.32 0.014 0.002 28.47 22.16 5.60 r V279 0.019 0.27 5.33 0.014 0.002 28.47 22.16 5.60 r V279 0.023 0.27 5.33 <t< td=""><td>654 SMO</td><td>V276</td><td>0.013</td><td>0.25</td><td>3.51</td><td>0.015</td><td>0.002</td><td>24.80</td><td>22.40</td><td>7.27</td><td><0.001</td><td>900.0</td><td>0,48</td></t<>	654 SMO	V276	0.013	0.25	3.51	0.015	0.002	24.80	22.40	7.27	<0.001	900.0	0,48
V2773 0.014 1.30 1.09 0.018 0.001 22.91 22.08 5.65 r V277 0.017 0.20 3.36 0.021 0.004 24.01 22.28 5.74 r V277 0.017 0.23 4.99 0.012 0.004 28.48 22.41 5.59 r V277 0.019 0.26 5.24 0.013 0.002 27.98 22.11 5.56 r V278 0.017 0.27 5.32 0.015 0.002 28.47 22.15 5.56 r V278 0.017 0.27 5.32 0.015 0.002 28.47 22.15 5.56 r V278 0.017 0.27 5.32 0.014 0.002 28.47 22.16 5.58 comb r V279 0.023 0.27 5.33 0.014 0.002 28.39 22.60 5.58 SMO V V V V	B66	Original sheet	0.016	0.19	3.14	0.022	0.002	23.38	21.64	5.33	0.002	0.003	1,42
r (top) V277 0.017 0.20 3.36 0.021 0.004 24.01 22.28 5.74 r (top) V274 0.020 0.23 4.99 0.012 0.004 28.48 22.41 5.59 r (top) V278 0.019 0.26 5.24 0.013 0.002 27.98 22.11 5.56 r (top) V278 0.017 0.27 5.32 0.015 0.002 28.47 22.15 5.56 r (top) V278 0.017 0.27 5.32 0.015 0.002 28.47 22.15 5.56 r (top) V279 0.019 0.27 5.32 0.014 0.002 28.47 22.16 5.60 r (top) V279 0.023 0.27 5.33 0.014 0.002 28.39 22.60 5.58 com) Charge No. Conjanal — S.	B66	V273	0.014	1.30	1.09	0.018	0.001	22.91	22.08	5.65	<0.001	0.003	1.49
r (top) V274 0.020 0.23 4.99 0.012 0.004 28.48 22.41 5.59 r (top) V275 0.019 0.26 5.24 0.013 0.002 27.98 22.11 5.56 r (top) V278 0.017 0.27 5.32 0.015 0.002 28.42 22.15 5.56 com)	B66	V277	0.017	0.20	3.36	0.021	0.004	24.01	22.28	5.74	<0.001	0.003	1.42
r (top) V278 0.019 0.26 5.24 0.013 0.002 27.98 22.11 5.56 r (top) V278 0.017 0.27 5.32 0.015 0.002 28.42 22.15 5.56 r (top) V278 0.017 0.27 5.32 0.015 0.002 28.47 22.05 5.58 r (top) V278 0.019 0.27 5.35 0.014 0.002 28.47 22.05 5.58 r (top) V279 0.029 0.27 5.35 0.014 0.002 28.39 22.60 5.58 r (top) V279 0.023 0.27 5.33 0.014 0.002 28.39 22.60 5.58 com) Charge No. Co N Sn As W V Al B SN SMO Original — 0.520 — — — — — — — — — — — — — — — — — — —	28Cr	V274	0.020	0.23	4.99	0.012	0.004	28.48	22.41	5.59	<0.001	0.005	0.72
r (top) V278 0.017 0.27 5.32 0.015 0.002 28.42 22.15 5.56 com) r (value) V278 0.017 0.27 5.32 0.015 0.002 28.47 22.05 5.58 com) r (top) V279 0.019 0.27 5.36 0.014 0.003 28.47 22.05 5.58 com) r (top) V279 0.023 0.27 5.33 0.014 0.002 28.39 22.06 5.60 5.58 com) Charge No. Co N Sn As W V Al B SMO Original — 0.520 — — — — — — — — — — — — — — — — — — —	28Cr	V275	0.019	0.26	5.24	0.013	0.002	27.98	22.11	5.56	<0.001	0.005	0,72
r (top) V278 0.017 0.27 5.35 0.015 0.002 28.47 22.62 5.58 com) r (top) V279 0.019 0.27 5.35 0.014 0.003 28.47 22.16 5.60 com) r (v279 0.023 0.27 5.33 0.014 0.002 28.39 22.60 5.58 com) Charge No. Co N Sn As W Y Al B SMO Original — 0.520 — — — — — — — — — — — — — — — — — — —	28Cr (top)	V278	0.017	0.27	5.32	0.015	0.002	28.42	22.15	5.56	<0.001	9000	0,79
com) v279 0.019 0.27 5.36 0.014 0.003 28.47 22.16 5.60 r V279 0.023 0.27 5.36 0.014 0.003 28.47 22.16 5.60 com) Charge No. Co N Sn W V Al B SMO Original — 0.520 — — — — — SMO V272 0.079 0.303 0.05 0.007 0.020 0.067 <0.001 0.0003 SMO V276 0.074 0.37 0.004 0.007 0.020 0.051 <0.001 0.0003 SMO V276 0.074 0.37 0.004 0.007 0.020 0.051 0.001 0.000 SMO V275 0.069 0.449 0.001 0.006 1.76 0.048 0.013 0.000 V273 0.065 0.453 0.001 0.005 1.87 0.041	28Cr	V278	0.017	0.27	5.32	0.015	0.002	28.47	22.62	5.58	<0.001	0.006	0,74
V279 0.019 0.27 5.36 0.014 0.003 28.47 22.16 5.60 V279 0.023 0.27 5.33 0.014 0.002 28.39 22.16 5.60 Charge No. Co N Sn As W V Al B Original — 0.520 — — — — — — V272 0.079 0.303 0.05 0.007 0.007 0.007 0.007 0.007 0.000 0.067 <0.001	(bottom)												`
r V279 0.023 0.27 5.33 0.014 0.002 28.39 22.60 5.58 com) Charge No. Co N Sn As W V Al B SMO Original — 0.520 — <td>28Cr (top)</td> <td>V279</td> <td>0.019</td> <td>0.27</td> <td>5.36</td> <td>0.014</td> <td>0.003</td> <td>28.47</td> <td>22.16</td> <td>5.60</td> <td>0.0000</td> <td>0.005</td> <td>0,71</td>	28Cr (top)	V279	0.019	0.27	5.36	0.014	0.003	28.47	22.16	5.60	0.0000	0.005	0,71
com) Charge No. Co N Sn As W V Al B SMO Original — 0.520 — <td< td=""><td>28Cr</td><td>V279</td><td>0.023</td><td>0.27</td><td>5.33</td><td>0.014</td><td>0.002</td><td>28.39</td><td>22.60</td><td>5.58</td><td><0.001</td><td>0.005</td><td>0,72</td></td<>	28Cr	V279	0.023	0.27	5.33	0.014	0.002	28.39	22.60	5.58	<0.001	0.005	0,72
SMO Original — 0.520 —	(bottom)												
SMO Original — 0.520 —		Charge No.	Co	Z	Sn	As	×	Λ	Al	В	0	PRE*	
SMO V272 0.079 0.303 0.05 0.007 0.020 0.067 <0.001 0.0003 SMO V276 0.074 0.37 0.004 0.007 0.020 0.051 <0.001	554 SMO	Original sheet		0.520			ì				1	63.8	
SMO V276 0.074 0.37 0.004 0.007 0.020 0.051 <0.001 0.0002 Original 0.069 0.449 0.001 0.006 1.76 0.048 0.013 0.0008 sheet V273 0.065 0.453 0.001 0.005 1.87 0.041 0.002 0.0002	554 SMO	V272	0.079	0.303	0.05	0.007	0.020	0.067	<0.001	0.0003		57.8	
Original 0.069 0.449 0.001 0.006 1.76 0.048 0.013 sheet V273 0.065 0.453 0.001 0.005 1.87 0.041 0.002	554 SMO	V276	0.074	0.37	0.004	0.007	0.020	0.051	<0.001	0.0002	0.0101	59.9	
V273 0.065 0.453 0.001 0.005 1.87 0.041 0.002	B66	Original sheet	0.069	0.449	0.001	900.0	1.76	0.048	0.013	0.0008		57.3	
	998	V273	0.065	0.453	0.001	0.005	1.87	0.041	0.002	0.0002		58.2	

,,,,					-						
B66	V277	0.074	0.373	0.001	0.008	1.73		<0.001	0.0008	0.018	57.0
28Cr	V274	0.075	0.483	0.004	0.004	0.020		<0.001	0.0002		61.5
28Cr	V275	0.081	0.53	0.002	0.005 0.020	0.020	0.056	<0.001	0.0002	0.0213	62.3
28Cr (top)	V278	0.088	0.72	0.005	0.008	0.070		<0.001	0.0002		68.5
28Cr	V278	0.088	0.72	900.0	9000	0.070		<0.001	0.0002		989
(bottom)								()))))))))))))))))))		10100	2
28Cr (top)	V279	0.090	0.71	0.005	0.007	0.020	0.063	<0.001	0.0002	0.0159	683
28Cr	V279	0.087	0.67	9000	0.008	0.020	0.063	<0.001	0.0002	0.0135	6 99
(bottom)								1);););

*PRE = Cr + 3,3Mo + 1.65W + 30N

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Macro-photographs of analysed ingots are shown in cross-section in Fig. 1, in which the volume proportion of equiaxed zone was measured, giving the results shown in Table 3. A equiaxed zone is fully developed in charges V274, V276, V278 and V279, while the other charges have a very low proportion of equiaxed zone, primarily caused by differences in tapping temperatures. In general, an increased casting temperature will result in an increased columnar crystal zone. Ingots of 28Cr (V278 and V279) have successfully been produced with a weakly segregated middle line, and really few pores (observed on the longitudinal sections of the ingots). Table 3 also gives the amount of measured intermetallic phase, which according to analysis by SEM-EDS (Table 4) is sigma phase (σ-phase). Vicker hardness is also included in Table 3. Hardness measurements were made on metallographic samples, using a load of 1 kg. Mean values were obtained from the five measurements in the intermediate area between the middle and the surface. The hardness is proportional to the N content in the steel.

15 Table 3

5

10

Table.					
Alloy	Charge	Proportion of uniform	Nitrogen	Amount of σ-	Hardness
	No.	axis zone	content	phase	(HV)
		(% by volume)	(% by weight)	(% by volume)	
654	V272	0	0.30	7.9	225
SMO					
654	V276	100	0.37	5.3	222
SMO					
B66	V273	15	0.45	1.4	236
B66	V277	4	0.37	0.5	209
28Cr	V274	100	0.48	2.1	230
28Cr	V275	16	0.53	0.9	229
28Cr	V278	100	0.72	<0.1	265
28Cr	V279	100	0.69	<0.1	262

Table 4 σ-phase composition in all ingots (% by weight), achieved from analysis by EDS/SEM

	COLUMNIA IN COL		, , , , , , , ,	-0),	*****	. 11 0 111 011	idiybib U	,	/
Alloy	Charge No.	Si	Cr	Mn	Fe	Ni	Mo	Cu	W
654 SMO	V272	0.9	30.9	3.0	33.8	13.1	18.4		
654 SMO	V276	0.6	30.7	3.2	32.9	13.8	18.7		
B66	V273	0.34	25.2	1.0	25.1	15.1	24.0		6.3
B66	V277	0.35	28.0	3.3	30.1	14.5	19.1	_	4.8
28Cr	V274	0.6	33.4	5.2	30.4	15.5	14.9		
28Cr	V275	0.8	33.0	5.9	27.2	15.7	17.4		
28Cr	V278	0.9	34.4	5.2	27.6	14.2	17.7		
28Cr	V279	0.7	34.6	5.5	28.0	14.8	16.1	0.4	

Casting structures are shown in Fig. 2. The amount of σ -phase in each produced ingot was measured from the surface to the middle of a cross-section according to cross index measurement (control instructions KF-10.3850/KFS 315, Avesta method) (see Table 3).

- Charges V272 and V276 (654 SMO) were high in σ-content, due to the all too low N content. For alloy 28Cr, the σ-phase content has been considerably decreased, thanks to the high N content of the steel. However, when N content is above 0.53 % by weight, a needle-shaped precipitation has formed at the grain boundaries. The precipitations are so thin that it has not been possible to determine their compositions. It is supposed that they are constituted by Cr₂N-nitrides. In Acta Polytechnica Scandinavia, Me No. 128, Espoo 1988, J. Tervo reported that Cr₂N-nitrides will be precipitated in 654 SMO, when N content is above 0.55 % by weight, and the nitrides are primarily formed at grain boundaries of similar appearance.
- Fig. 3 shows the micro-structure achieved in annealing, for some representative alloys. In the structures of charges V272-V277, σ-phase is maintained. Due to the segregation effect, the annealing temperature used (1180 °C) may still be too low to remove the intermetallic phases. A micro-structure essentially void of intermetallic phases, for example σ-phase, should not have a value of more than 0.6 in cross index measurement according to the measuring method above. In the experiments with 28Cr, the needle-shaped phase however disappeared after solution annealing. A fully austenitic structure was obtained for the high N charges (V278 and V279).

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REMELTING BY SPOT WELDING WITH TIG

As the tapping temperatures varied for the various ingots, it was hard to directly compare the segregation levels of alloys 28Cr (according to the present invention), and 654 SMO and B66, respectively. Accordingly, remelting was made by using spot welding with TIG on each sample of 28Cr, as well as on original sheets of 654 SMO and B66, respectively. Identical welding parameters were used (I = 100 A, V = 11 V, t = 5 s, protective gas Ar at a flow of 10 l/min, and the same arc length.)

The segregation level of alloy 28Cr was compared to that of 654 SMO and B66, respectively. The distribution coefficient K was determined as is shown in Table 5. Si and Mo are the alloying elements of highest coefficient, i.e. they are the most segregating ones. The quotient is markedly lower for W, but it is still higher than the one for Cr. Accordingly, it is beneficial to have high contents of Cr, that exhibits the lowest tendency for segregation, and to keep the contents of Mo and silicon very low.

15 Here, Tungsten takes up an intermediate level.

Table 5 EDS/WDS analyses for determination of the distribution coefficient K K = C_{ID}/C_D . C_{ID} is the element content in the interdentritic centre; C_D is the element content in the dendritic centre.

					T T T T T T T T T T T T T T T T T T T				
Alloy \ K	Si	Cr	Mn	Fe	Ni	Cu	Mo	W	N
B66	4.06	1.06	1.26	0.88	0.98	1.25	1.70	1.14	1.18
654 SMO	3.08	1.02	1.14	0.84	0.86	1.13	1.73		1.27
28CR-V274	1.96	1.02	1.27	0.87	0.99	1.35	1.68		1.07
28CR-V275	1.78	1.02	1.27	0.85	0.99	1.41	1.84		1.20
28CR-V278	1.96	1.02	1.24	0.87	1.00	1.14	1.58		1.24
28CR-V279	1.80	1.01	1.34	0.85	1.00	1.37	1.80		1.19

CORROSION TESTS

Double samples were taken from the bottom part, close to the longitudinal section ingot surfaces, and were solution annealed at 1180 °C for 40 min, followed by quenching in water. The pitting temperature was thereafter measured on sample surfaces that had been ground by 320 grit grinding paper. The analysis was made in accordance with the standard ASTM G510 in 3M NaBr solution. The current density was potentiostatically monitored at +700 mV SCE, during a temperature scanning from 0 °C to 94 °C. The critical pitting temperature (CPT) was defined as the temperature at which the current

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density exceeded $100 \,\mu\text{A/cm}^2$, i.e. the point at which local pitting first took place. The results from the pitting test are shown in Table 6.

Table 6
Critical pitting temperature (CPT) for various alloys

Alloy	Charge no.		CPT (°C)
		Test 1	Test 2	Mean value
654 SMO	V276	79.1	81.8	80.5
B66	V277	>87.0	85.4	>86.2
28Cr	V274	67.5	61.4	64.5
28Cr	V275	68.0	59.6	63.9
28Cr	V278	>93.0	70.5	>81.8
28Cr	V279	79.1	89.2	84.2

5 The results show that pitting resistance is high for 28Cr (V278-9), and in some cases better than for the commercial steels.

CONCLUSIONS

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Thanks to the high levels of Cr and manganese, a good solubility of N is achieved in alloy 28Cr. This good solubility of N, based on the higher Cr content, enables a lowering of the Mo content while all in all maintaining the PRE-value at the same level as for 654 SMO.

The increased N content lowers the amount of sigma phase markedly. In particular in the area of 0.67-0.72 % by weight of N, the alloy 28Cr exhibits a fully austenite structure already in the casting stage, with very little needle-shaped nitrides formed at the grain boundaries, and being nearly free form sigma phase. After solution annealing at 1180 °C for 40 min, the nitrides could be completely removed.

The alloy 28Cr with the preferred N content has a good pitting resistance, similar to that of 654 SMO and B66.

The austenitic stainless steel according to the invention is accordingly very well adapted, in various processed forms, such as sheets, bars and pipes, for use in aggressive environments in chemical industry, energy plants and various seawater applications.

CLAIMS

1. An austenitic stainless steel, characterised in that is has a composition of, in % by weight:

max 0.03 C

5 max 0.5 Si

max 6 Mn

28-30 Cr

21-24 Ni

4-6% (Mo + W/2), the content of W being max 0.7

10 0.5-1.1 N

25

30

max 1.0 Cu

balance iron and impurities at normal contents originating from the production of the steel.

- 2. A steel according to claim 1, characterised in that it contains 0.015-0.025 C.
 - 3. A steel according to claim 2, characterised in that it contains 0.020 C.
- 4. A steel according to claim 1, characterised in that it contains max 0.3, preferably max 0.25 Si.
 - 5. A steel according to claim 1, characterised in that it contains at least 4 Mn.
 - 6. A steel according to claim 5, characterised in that it contains 4.5-5.5, preferably about 5.0 % Mn.
 - 7. A steel according to claim 1, characterised in that it contains 28.0-29.0, preferably 28.5 Cr.
 - 8. A steel according to claim 1, characterised in that it contains 22-23, preferably 22.0-22.6 Ni.
- 9. A steel according to claim 1, characterised in that it contains 5-6, preferably about 5.5 Mo.

- 10. A steel according to claim 9, characterised in that it contains max 0.5, preferably max 0.3, and most preferred max 0.1 W.
- 11. A steel according to claim 1, characterised in that it contains at least 0.6 N.
 - 12. A steel according to claim 11, characterised in that it contains 0.6-0.8 N.
- 13. A steel according to claim 1, characterised in that it contains at least 0.5, preferably 0.7-0.8 Cu.
 - 14. A steel according to claim 1, characterised in that it optionally also may contain one or more elements that increase hot ductility, such as:

max 0.005 B

max 0.1 Ce + La

max 0.05 A1

max 0.01 Ca

max 0.01 Mg

- 15. A steel according to claim 1, characterised in that it contains Cr, Mo and N at amounts such that a PRE-value of at least 60 can be obtained, where PRE=Cr+3.3Mo+1.65W+30N.
- 16. A steel according to claim 15, characterised in that the PRE-value is at least 64, preferably at about 66.
 - 17. A steel according to claim 1, characterised in that it contains: max 0.3 Si

5-6 (Mo+W/2), whereof the amount of W is max 0.7, and

- 30 0.6-0.9 N, and in that after heat treatment at a temperature of 1150-1220 °C, the steel has a homogeneous microstructure mainly consisting of austenite and being essentially void of harmful amounts of secondary phases.
- 18. A steel product, characterised in that it has been produced from a steel having a composition according to any one of the preceding claims, where the production comprises continuous casting of said steel for forming flat or long products.

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19. A steel product according to claim 18, characterised in that without any remelting, it has been hot rolled to a final dimension of max 50 mm at a reduction rate of at least 1:3, and that it has a micro-structure having a low level of segregation.

20. A steel product according to claim 19, characterised in that the steel contains:

max 0.3 Si

5

5-6 (Mo+W/2), whereof the amount of W is max 0.7, and 0.6-1.1 N, and in that said steel product after heat treatment at a temperature of 1150-1220 °C, has a microstructure mainly consisting of austenite which is essentially void of harmful amounts of secondary phases.

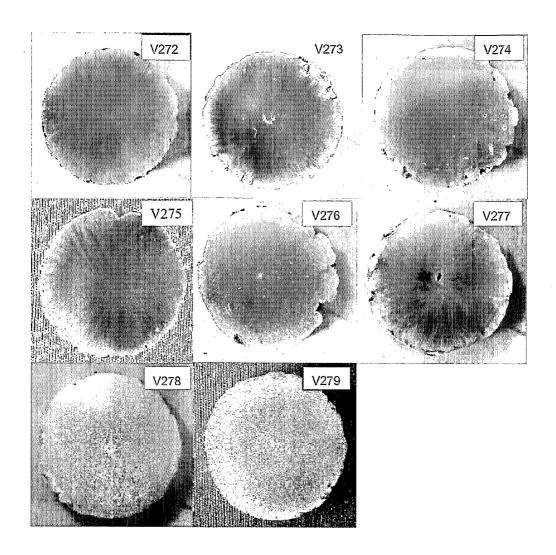


Fig. 1

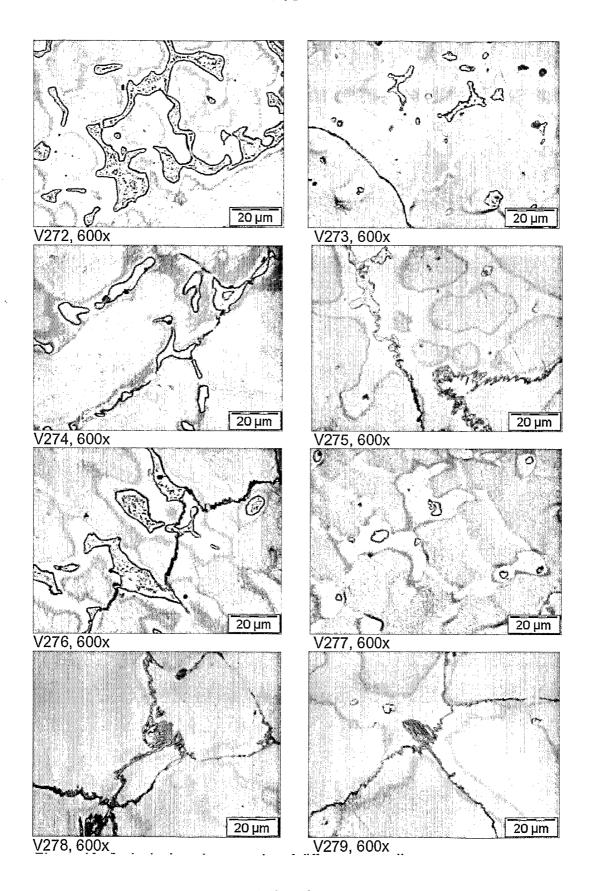


Fig. 2

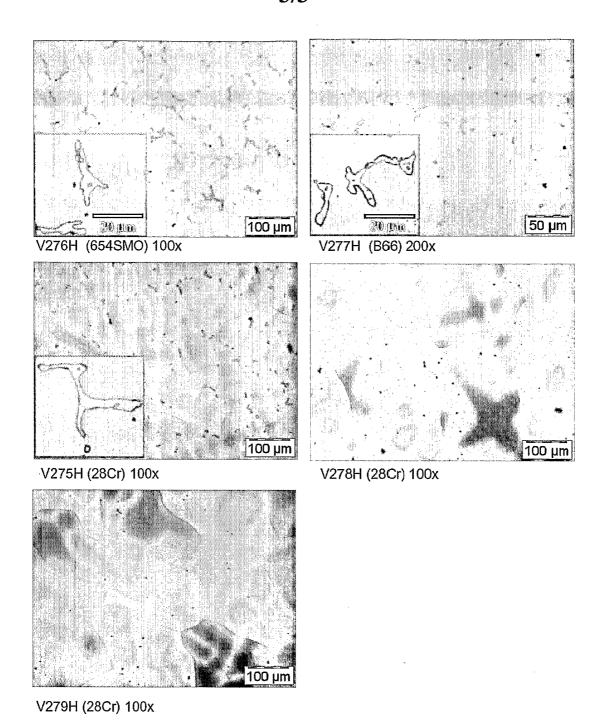


Fig. 3

International application No.

PCT/SE2005/002057

A. CLASSIFICATION OF SUBJECT MATTER

IPC: see extra sheet

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)

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

SE,DK,FI,NO classes as above

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

EPO-INTERNAL, WPI DATA, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DATABAS WPI Week 199426 Derwent Publications Ltd., London, GB; Class M27, AN 1994-211231 & JP 6145913 A (SUMITOMO METAL IND LTD), 27 May 1994 (1994-05-27) abstract, page 91 - page 92, see for example steel no 1,2,7 and 17	1-20
A	EP 0507229 A1 (THYSSEN SCHWEISSTECHNIK GMBH), 7 October 1992 (07.10.1992), page 2, 1ine 1 - line 48, Table 1	1-20

χ	Further documents are listed in the continuation of Box C.	L
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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
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2 9 -03- 2006

"&" document member of the same patent family

Date of mailing of the international search report

Date of the actual completion of the international search

28 March 2006

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Telephone No. +46 8 782 25 00

Form PCT/ISA/210 (second sheet) (April 2005)

International application No.
PCT/SE2005/002057

	PC1/3E2003,	002037
C (Continu	ation). DOCUMENTS CONSIDERED TO BE RELEVANT	
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0342574 A1 (THYSSEN EDELSTAHLWERKE AG), 23 November 1989 (23.11.1989), Table 1, leg.nr 9, 11,15-18	1-20
A	US 20030143105 A1 (BAHAR ET AL), 31 July 2003 (31.07.2003), Table 1, nr 3,8,10	1-20
A	EP 0438992 A1 (AVESTA AKTIEBOLAG), 31 July 1991 (31.07.1991), page 1 - page 5, Table 2	1-20
A	DE 3729577 C1 (THYSSEN EDELSTAHLWERKE AG), 1 Sept 1988 (01.09.1988), page 2 - page 3	1-20
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International application No. PCT/SE2005/002057

International patent classification (IPC)

C22C 38/44 (2006.01) C22C 38/58 (2006.01)

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Cited literature, if any, will be enclosed in paper form.

INTERNATIONAL SEARCH REPORT Information on patent family members

31/12/2005

International application No. PCT/SE2005/002057

		•				
EP	0507229	A1	07/10/1992	CA CS DE FI NO PL	2064925 A 9201016 A 4110695 A 921458 A 921275 A 294087 A	04/10/1992 14/10/1992 08/10/1992 04/10/1992 05/10/1992 14/12/1992
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