



(11) **EP 3 551 775 B1**

(12) **EUROPEAN PATENT SPECIFICATION**

(45) Date of publication and mention of the grant of the patent:

23.06.2021 Bulletin 2021/25

(21) Application number: **17808459.6**

(22) Date of filing: **01.12.2017**

(51) Int Cl.:

C22C 33/02 (2006.01) **B22F 9/08** (2006.01)
C22C 38/40 (2006.01) **C22C 38/44** (2006.01)
C22C 38/00 (2006.01) **C22C 38/02** (2006.01)
C22C 38/04 (2006.01) **C22C 38/34** (2006.01)
C22C 38/42 (2006.01)

(86) International application number:

PCT/EP2017/081234

(87) International publication number:

WO 2018/104179 (14.06.2018 Gazette 2018/24)

(54) **STAINLESS STEEL POWDER FOR PRODUCING DUPLEX SINTERED STAINLESS STEEL**

EDELSTAHPULVER ZUR HERSTELLUNG VON DUPLEXGESINTERTEM EDELSTAHL

POUDRE D'ACIER INOXYDABLE POUR LA PRODUCTION D'ACIER INOXYDABLE DUPLEX FRITTÉ

(84) Designated Contracting States:

AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR

(30) Priority: **07.12.2016 EP 16202574**

(43) Date of publication of application:

16.10.2019 Bulletin 2019/42

(73) Proprietor: **Höganäs AB (publ)**

263 83 Höganäs (SE)

(72) Inventor: **BADWE, Sunil**

Export, PA 15632 (US)

(56) References cited:

EP-A1- 0 167 822 EP-A1- 1 561 834
US-A- 4 581 202

EP 3 551 775 B1

Note: Within nine months of the publication of the mention of the grant of the European patent in the European Patent Bulletin, any person may give notice to the European Patent Office of opposition to that patent, in accordance with the Implementing Regulations. Notice of opposition shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

Description

TECHNICAL FIELD

5 **[0001]** Embodiments of the present invention may provide a new stainless steel powder suitable for manufacturing of duplex sintered stainless steels. Embodiments of the present invention may also relate to a method for producing the stainless steel powder, the duplex sintered stainless steel as well as methods for producing the duplex sintered stainless steel.

10 BACKGROUND

[0002] Duplex stainless steels have been known to the industry for more than 60 years. They are widely used in heat-treated cast, wrought and gas atomized powder forms, in many applications that require a combination of high strength and high corrosion resistance. However, they are unavailable today, in the water atomized powder form for use in press and sinter applications.

15 **[0003]** Common uses for duplex stainless steels include chemical process plants pipeline, petrochemical industry, power plants and automobiles. They are also used in food processing industry, pharmaceutical process components, paper and pulp industry, in desalination plants and in the mining industry. Duplex stainless steels are known for their high resistance to inter granular corrosion (IGC) and stress corrosion cracking (SCC) in chloride media. Chloride is severe challenge that leads to rapid corrosion media for iron-based alloys.

20 **[0004]** High strength and high corrosion resisting properties in duplex stainless steel are believed to be acquired due to a presence of ferrite and austenite phases in equal amounts. Such structure is generally achieved by using a balance of austenite stabilizers, e.g., nickel (Ni), manganese (Mn), carbon (C), nitrogen (N), copper (Cu) and cobalt (Co), and ferrite stabilizers, e.g., chromium (Cr), silicon (Si), molybdenum (Mo), tungsten (W), titanium (Ti) and niobium (Nb).

25 **[0005]** As mentioned previously, the high strength and high corrosion resistance of duplex stainless steel is believed to come from a balance of ferrite and austenite in the microstructure. The microstructure depends not only on the chemistry but also on the heat treatment carried out on the material. All duplex steel compositions today make use of N in the chemistry, as N is a strong austenite stabilizer. N, when present in the alloy along with Cr, poses problem of forming nitrides which are deleterious to the properties such as strength and corrosion resistance. Further, during welding duplex stainless steels, an intermetallic phase known as "Sigma" is formed in a heat affected zone (HAZ) due to slower cooling rates. This Sigma phase is a hard, supersaturated, intermetallic phase containing Cr and Mo. The area around the Sigma phase is depleted of Cr and Mo and becomes weak and less resistant to corrosion. Often duplex stainless steels need annealing and quenching process to reduce or eliminate this Sigma phase.

30 **[0006]** In wrought or cast duplex stainless steels, the steel is solidified as ferritic steel and the austenite phase is precipitated out from ferrite during cooling of the alloy. The cooling rate is critical after casting or at any heat treatment, as the cooling rate determines the percentage of austenite and any intermetallic phases, precipitated within the structure.

35 **[0007]** Although wrought duplex stainless steels, in particular 'hot rolled' duplex stainless steels, have been common in industrial use since 1930s, they were hardly used in the Powder Metallurgy (PM) industry. There are a few applications where gas atomized duplex stainless steel powders are used in hot isostatic pressed (HIP) condition. Powders produced by gas atomizing have spherical morphology. Such powders are less suitable for conventional press and sinter applications. Due to the spherical shape, they have insufficient green strength, which is required to handle green press and sinter parts. Irregular shaped powders, such as those produced with water atomization, have much higher green strength as the irregular shape of the powders tends to bind together the powder particles. Currently there is no water atomized stainless steel powder available for producing sintered duplex stainless steel components. The current chemical compositions used in gas atomized powders, and also in wrought steels, use N as a major alloying element to achieve austenite-ferrite balance and achieve required mechanical strength. Inclusion of N in the powder increases the hardness of the powder reducing the compressibility in conventional press and sinter applications. This may result in reduced green density and subsequently reduced sinter density.

40 **[0008]** There have been several attempts to develop sintered duplex stainless steels made from water atomized powders. Lawley et al¹ attempted to develop equivalent grades of AISI 329 and AISI 2205 with maximum tensile strength of 578 MPa. Dobrzanski et al² mixed ferritic and austenitic powders to produce duplex structure with tensile strength 650 MPa. The same group also studied the corrosion properties of duplex stainless steel with electrochemical method and concluded that the duplex stainless steels show better corrosion resistance than their austenitic counterpart³. Due to their high alloy content, these steels are sensitive to the composition and also the processing parameters. These alloys form intermetallic phases known as sigma, chi and gamma prime which are rich in Mo, W, N, Ni and Cr and reduce both mechanical properties and corrosion properties. Sigma phase forms in a temperature range 700°C to 1000°C whereas Chi phase forms within range 300°C to 450°C. The Gamma (austenite) phase may start forming at around 600°C.

45 ¹A. Lawley, E. Wagner, C.T. Schade, Advances in Powder Metallurgy and Particulate Materials 2005 Part 7 pp 78-89

²L.A. Dobrzanski, Z. Brytan, M. Actis Grande, M. Rosso, Archives of Materials Science and Engineering, Vol 28 Iss 4, April 2007 PP 217-223

³L.A. Dobrzanski, Z. Brytan, M. Actis Grande, M. Rosso, Journal of Achievements in Materials and Manufacturing Engineering, Vol 17 Iss 1-2 pp 317-320

5 **[0009]** Typical composition of wrought duplex stainless steel is Fe with 21-23wt% Cr, 4.5-6.5wt% Ni, 2.5-3.5wt% Mo, and 0.08-0.2wt% N, such as for SAF 2205. There are numerous patents for duplex stainless steel composition close to this composition. Almost all of the duplex stainless steels rely on the N content for increased corrosion resistance and increased strength. So far the commercial uses of sintered powder metallurgy (PM) duplex stainless steels are limited to the use of gas atomized fine powders that can be used for mainly HIP process. The main obstacle in using low cost water atomized powders for conventional PM use is increased N and possibility of intermetallic and carbide precipitation due to cooling rate during the sintering. Also conventional sintering needs some wetting agents or low temperature melting constituents to increase free energy and accelerate the kinetics of austenite phase precipitation within ferritic matrix.

[0010] In the patent literature there are some documents disclosing sintered duplex stainless steel structures.

15 **[0011]** SE538577C2 (Erasteel) discloses a sintered duplex stainless steel made from gas atomized powder and having a chemical composition with a max 0.030wt% C, 4.5-6.5wt% Ni, 0.21-0.29wt% N, 3.0-3.5wt% Mo, 21-24wt% Cr, and optionally one or more of 0-1.0wt% Cu, 0-1.0wt% W, 0-2.0wt% Mn, 0-1.0wt% Si wherein N is equal or greater than 0.01*wt%Cr and the remaining elements are Fe and unavoidable impurities.

20 **[0012]** EP0167822A1 (Sumitomo) discloses a sintered stainless steel comprising a matrix phase and a dispersed phase and a process for manufacturing. The dispersed phase is an austenite metallurgical structure and is dispersed throughout the matrix phase, which is comprised of an austenitic metallurgical structure having a steel composition different from that of the dispersed phase or a ferritic-austenitic duplex stainless steel.

25 **[0013]** JP5263199A (Sumitomo) discloses production of a sintered stainless steel comprising a matrix phase and a dispersing phase. The method includes mixing a ferritic stainless steel powder with a powder selected from an austenitic stainless steel powder, an austenitic-ferritic duplex stainless steel powder, an austenitic-martensitic duplex stainless steel powder and austenitic-ferritic-martensitic stainless triple phase stainless steel powder. The powder mixture being compacted and sintered.

[0014] EP0534864B1 (Sumitomo) discloses a sintered stainless steel having a content of N of 0.10-0.35wt% and made from gas atomized steel powder having the same chemical composition as the sintered stainless steel.

30 SUMMARY

[0015] Almost all duplex grades available have N content between 0.18- 0.40wt% in order to balance austenite-ferrite balance in the structure and increase the strength. Although N content helps the above properties, it can pose hurdles in post processing, such as heat treatment and welding operations, by forming chromium nitrides, which limits the use of duplex stainless steels in many applications. In powder form, N increases the powder hardness making it less suitable for press and sinter applications.

35 **[0016]** Embodiments of the invention overcome the problem with nitrides by avoiding the use of N in the chemistry, for example, having less than 0.10 wt% N or less than 0.07 wt% N, or less than 0.06 wt% N, or less than 0.05 wt% N, or less 0.04 wt% N, or less than 0.03 wt% N, and achieving phase balance and strength by alternative elements. Embodiments of the invention may enable production of water atomized powder with moderate compressibility for use in conventional press and sinter applications. Embodiments of this composition may also reduce precipitation of a deleterious 'Sigma' phase; irrespective of rate of cooling during sintering or annealing, mainly due to lower Mo content. Thus, minimizing post sintering heat treatments necessary to eliminate "Sigma" phase and minimizing sigma phase precipitation during welding.

45 **[0017]** Embodiments of the composition may offer similar advantages when formed by gas atomization.

[0018] Other than conventional PM, embodiments of the composition yield similar properties when processed with casting, direct metal deposition and additive manufacturing techniques.

50 DETAILED DESCRIPTION

[0019] One object of certain embodiments of the invention is to provide an alloy powder for conventional PM that will produce a duplex structure during a sintering cycle. Another object of certain embodiments of the present invention is to provide a duplex sintered stainless steel.

55 **[0020]** Another object of certain embodiments of the present invention is to obtain at least 35% higher tensile strength than ferritic steels such as 430L and double the corrosion resistance compared to austenitic steels such as 316L.

[0021] Still another object of certain embodiments of the present invention is to provide a method for producing a duplex sintered stainless steel without the need of post sintering heat treatment.

EP 3 551 775 B1

[0022] The above objectives may be accomplished by the following aspects and embodiments.

[0023] In a first aspect of the present invention there is provided a stainless steel powder comprising, or consisting of, in weight percent:

5 up to 0.1% of C,
0.5-3% of Si,
up to 0.5% of Mn,
20-27% of Cr,
3-8% of Ni,
10 1-6% of Mo,
up to 3% of W,
up to 0.1% N,
up to 4% of Cu,
up to 0.04% of P,
15 up to 0.04% of S,
unavoidable impurities up to 0.8%, whereof Sn may be present up to 0.2%,
optionally one or more of up to 0.004% B, up to 1% Nb, up to 0.5% Hf, up to 1% Ti, up to 1% Co,
rest Fe.

20 **[0024]** The unavoidable impurities do not include the listed elements of C, Si, Mn, Cr, Ni, Mo, W, N, Cu, P, S, B, Nb, Hf, Ti, or Co. Unavoidable impurities may include impurities that cannot be controlled, or controlled with difficulty, during manufacture of steels. These can come from the raw materials used and also from the process. These include, Al, O, Mg, Ca, Ta, V, Te, or Sn. The unavoidable impurities may be up to 0.8%, up to 0.6%, up to 0.3%. An unavoidable impurity may be O. O may be present up to 0.6%, up to 0.4%, or up to 0.3%. Another unavoidable impurity may be Sn present
25 up to 0.2%, content of Sn above 0.2% is in this context not regarded as an unavoidable impurity and thus will be regarded as intentionally added.

[0025] In a preferred embodiment of the first aspect there is provided a stainless steel powder consisting of, in weight percent:

30 up to 0.06% of C,
1-3% of Si,
up to 0.3% of Mn,
23-27% of Cr,
4-7% of Ni,
35 1-3% of Mo,
0.8-1.5% of W,
up to 0.07% N,
1-3% of Cu,
up to 0.04% of P,
40 up to 0.03% of S,
unavoidable impurities up to 0.8%, whereof Sn may be present up to 0.2%,
optionally one or more of up to 0.004% B, up to 1% Nb, up to 0.5% Hf, up to 1% Ti, up to 1% Co,
rest Fe.

45 **[0026]** In another preferred embodiment of the first aspect there is provided a stainless steel powder comprising in weight percent:

up to 0.03% of C,
1.5-2.5% of Si,
50 up to 0.3% of Mn,
24-26% of Cr,
5-7% of Ni,
1-1.5% of Mo,
1-1.5% of W,
55 up to 0.06% N,
1-3% of Cu,
up to 0.02% of P,
up to 0.015% of S,

unavoidable impurities up to 0.8%, whereof Sn may be present up to 0.2%, optionally one or more of up to 0.004% B, up to 1% Nb, up to 0.5% Hf, up to 1% Ti, up to 1% Co, rest Fe.

5 **[0027]** In embodiments of the first aspect the powder is ferritic. For example, 99.5% ferritic. Slight amounts of austenite, e.g., up to 0.5% may be tolerated.

[0028] In embodiments according to the first aspect the powder is produced by water atomization.

10 **[0029]** In embodiments of the first aspect the powder is produced by gas atomization. In embodiments of the first aspect the particle size of the powder is between 53 microns and 18 microns such that at least 80wt% of the particles are less than 53 microns and at most 20wt% of the particles are less than 18 microns.

[0030] In embodiments of the first aspect the particle size of the powder is between 26 microns and 5 microns such that at least 80wt% of the particles are less than 26 microns and at most 20wt% of the particles are less than 5 microns.

[0031] In embodiments of the first aspect the particle size of the powder is between 150 microns and 26 microns such that at least 80wt% of the particles are less than 150 microns and at most 20wt% of the particles are less than 26 microns.

15 **[0032]** In a second aspect of the present invention there is provided a method of producing a stainless steel powder according to the first aspect comprising the steps of:

- providing a molten metal of having a chemical composition corresponding to the chemical composition of the stainless steel powder according to the first aspect;
- 20 - subjecting a stream of the molten metal to water atomization; and
- recovery of the obtained stainless steel powder.

[0033] In a third aspect of the present invention there is provided a sintered duplex stainless steel having a chemical composition according to the first aspect and embodiments thereof.

25 **[0034]** In embodiments of the third aspect the Ni equivalent (Ni_{eq}) is such that $5 < Ni_{eq} < 11$ and the Cr equivalent (Cr_{eq}) is such that $27 < Cr_{eq} < 38$.

[0035] In embodiments of the third aspect the pitting resistance equivalent number (PREN) is $28 < PREN < 33$.

[0036] In embodiments of the third aspect, the microstructure of the sintered duplex stainless steel is characterized by austenite phase precipitated within ferrite phase.

30 **[0037]** In embodiments of the third aspect, the microstructure of the sintered duplex stainless steel contains 30-70% austenite and 30-70% ferrite. In embodiments of the third aspect, the microstructure of the sintered duplex stainless steel contains at least 99.5% austenite and ferrite, for example, at least 99.8% austenite and ferrite. The percentage of austenite and ferrite may be determined by ASTM E 562-11 and ASTM E 1245 -03.

[0038] In embodiments of the third aspect the microstructure of the sintered duplex stainless steel is characterized by being free from sigma phases and nitrides, for example, having less than 1% of sigma phases and nitrides.

35 **[0039]** In a fourth aspect of the present invention there is provided a method for producing a sintered stainless steel comprising the steps of:

- providing a stainless steel powder according to the first aspect,
- 40 - optionally mixing the stainless steel powder with a lubricant and optionally other additives,
- subjecting the stainless steel powder or the mixture to a consolidation process forming a green component,
- subjecting the compacted green component to a sintering step in an inert or reducing atmosphere or in vacuum at a temperature between 1150°C to 1450°C, preferably at a temperature between 1275°C to 1400°C for a period of time of 5 minutes to 120 minutes ,
- 45 - subjecting the sintered component to a cooling step down to ambient temperature.

[0040] Examples of an inert atmosphere include argon, and vacuum with argon backfill.

50 **[0041]** An example of a reducing atmosphere is a hydrogen atmosphere, an atmosphere of a mixture of hydrogen and nitrogen, or an atmosphere of dissociated ammonia. In limited examples, carbon dioxide or carbon monoxide atmospheres may be used.

[0042] In embodiments of the fourth aspect said consolidation process includes the steps of:

- uniaxial compaction at a compaction pressure of up to 900 MPa in a die to form a green component,
- 55 - ejecting the obtained compacted green component from the die.

[0043] In embodiments of the fourth aspect said consolidation process includes one of: Metal Injection Molding (MIM), Hot Isostatic Pressing (HIP) or Additive Manufacturing techniques such as Binder Jetting.

[0044] Methods according to the fourth aspect may include one of Laser Powder Bed Fusion (L-PBF), Direct Metal

Laser Sintering (DMLS) or Direct Metal Deposition (DMD).

[0045] In embodiments of the fourth aspect forced cooling or quenching is excluded from the cooling step.

Effect of alloying elements

5 [0046] The effect of common alloying elements in stainless steels is well known. Cr is a major element in stainless steels which forms a Cr₂O₃ layer on the surface which then prevents further oxygen passing the layer, therefore providing an increased corrosion resistance. Ni is another major element which affects the properties of stainless steel. Ni increases the strength and toughness of the steel and also when present with Cr, enhances the corrosion resistance. Mo and W both impart the strength and toughness when present along with Ni. Mo also enhances the corrosion resistance along with Cr and Ni. Si acts as deoxidizer preventing O combining in the steel during melting, Si is also a strong ferrite former. Cu is austenite stabilizer. Cu also increases the corrosion resistance of stainless steel. Especially in conventional PM, Cu helps sintering by promoting liquid phase sintering.

15 [0047] Embodiments of the invention provide a powder suitable for producing sintered duplex stainless steel, as well as the sintered stainless steel. The powder and the sintered stainless steel having a low or neglectable content of N. This eliminates the problem of formation of deleterious nitrides during fabrication of the sintered stainless steel. The sintered stainless steel is preferably produced from a compacted and sintered water-atomized powder since the low N content makes it possible to produce water-atomized powder with reasonable compressibility.

20 [0048] Mo is normally present in stainless steel as it strongly promotes the resistance to both uniform and localized corrosion. Mo strongly stabilizes ferritic microstructure. At the same time Mo is prone to precipitate Mo rich "Sigma" and "Chi" phases at ferrite- austenite grain boundary. These are deleterious phases and affect strength and corrosion resistance adversely. However, due to lower Mo content in embodiments of the powder of the present invention, the possibility of forming sigma phase at any cooling rate is reduced, eliminating or reducing the need for the post processing heat treatment of annealing. This also means that the sigma phase will not likely form during welding operation, which is a common fabrication process for duplex stainless steels.

25 [0049] Cr gives stainless steels their basic corrosion resistance and increases the resistance against high temperature corrosion.

[0050] Ni promotes an austenitic microstructure and generally increases ductility and toughness. Ni has also a positive effect as it reduces the corrosion rate of stainless steels.

30 [0051] Cu promotes an austenitic microstructure. The presence of Cu in the powder of the present invention facilitates the sintering process by enabling liquid phase sintering.

[0052] W is expected to improve the resistance against pitting corrosion.

[0053] Si increases strength and promotes a ferritic microstructure. It also increases oxidation resistance at high temperatures and in strongly oxidizing solutions at lower temperatures.

35 [0054] When present in the powder according to certain embodiments of the present invention B, Nb, Hf, Ti, Co may enhance the properties. B when added in small % may help in liquid phase sintering. However, excess B, if present, may form borides, which are deleterious to both mechanical, and corrosion properties. Nb and Hf when present may stabilize the microstructure by preferentially combining with carbon forming fine carbides freeing Cr for the corrosion resistance. Ti in stainless steels may increase the tensile strength and toughness. Co increases the high temperature mechanical properties.

40 [0055] Elements such as C, Mn, S and P should be kept at a level as low as possible in the powder of embodiments of the present invention as they may have a negative effect to various extent on compressibility of the powder and/or mechanical and corrosion preventive properties of the sintered component. Other elements, here designated as unavoidable impurities, may be tolerated up to a content of 0.8% by weight of the powder according to the present invention.

45 [0056] The composition of the powder according to embodiments of the present invention is designed such that the produced powder will have fully (e.g., at least 99.5%) ferritic structure in the powder form and austenitic phase is precipitated out during sintering cycle. This will allow controlling the ratio of ferrite and austenite by adjusting the sintering parameters.

50 [0057] Ni and Cr equivalents are calculated based on following empirical formulae:

$$Cr_{eq} = Cr + 2Si + 1.5Mo + 0.75W$$

55
$$Ni_{eq} = Ni + 0.5Mn + 0.3Cu + 25N + 30C$$

[0058] Where Cr, Ni, etc. are the level of each element in the alloy in weight %.

[0059] Further Pitting Resistance Equivalent Number is calculated as:

$$\text{PREN} = \text{Cr} + 3.3\text{Mo} + 16\text{N}$$

[0060] Where Cr, Mo and N are the level of each element in the alloy in weight %.

[0061] The composition is targeted such that $5 < \text{Ni}_{\text{eq}} < 11$ and $27 < \text{Cr}_{\text{eq}} < 38$. This places the alloy in at the border of Ferritic - Duplex region on Schaeffler Diagram. At this point the alloy is almost entirely ferritic (e.g., at least 99.5%). Elements like Mo, W and Si are supersaturated in the ferritic matrix.

[0062] The powder of embodiments of the present invention may be produced by conventional powder manufacturing processes. Such processes may encompass melting of the raw materials followed by water or gas atomization, forming a so called prealloyed powder wherein all elements are homogeneously distributed within the iron matrix. A major advantage with a prealloyed powder in contrast to a premixed powder, wherein two or more powders are mixed together, is that segregation is avoided. Such segregation may cause variation in mechanical properties, corrosion resistance etc.

[0063] When used for the production of sintered components, the powder of embodiments of the present invention may be compacted in a conventional uniaxial compaction equipment at a compaction pressure up to 900 MPa.

[0064] Suitable particle size distribution of the stainless steel powder to be used at conventional uniaxial compaction is such that the particle size of the powder is between 53 microns and 18 microns such that at least 80wt% of the particles are less than 53 microns and at most 20wt% of the particles are less than 18 microns. Before compaction, the powder of embodiments of the present invention may be mixed with conventional lubricants, such as, but not limited to, Acrawax, Lithium Stearate, Intralube at a content up to 1wt%. Other additives mixed in, up to 0.5wt%, may be machinability enhancing agents such as CaF_2 , muscovite, bentonite or MnS.

[0065] Other methods of consolidation techniques may be utilized such as Metal Injection Molding (MIM), Hot Isostatic Pressing (HIP), extrusion or Additive Manufacturing techniques such as Binder Jetting, Laser Powder Bed Fusion (LPBF), Direct Metal Laser Sintering (DMLS) or Direct Metal Deposition (DMD)

[0066] In a MIM process, suitable particle size distribution of the stainless steel powder to be used is such that the particle size of the powder is between 26 microns and 5 microns such that at least 80wt% of the particles are less than 26 microns and at most 20wt% of the particles are less than 5 microns.

[0067] In a HIP or extrusion process suitable particle size distribution of the stainless steel powder to be used is such that the particle size of the powder is between 150 microns and 26 microns such that at least 80wt% of the particles are less than 150 microns and at most 20wt% of the particles are less than 26 microns.

[0068] The particle size distribution may be measured by a conventional sieving operation according to ISO 4497:1983 or by laser diffraction (Sympatec) according to ISO 13320:1999.

[0069] After compaction or consolidation, the compacted or consolidated body is subjected to a sintering process at sufficiently high temperatures in the range of 1150°C to 1450°C, preferably at sufficiently high temperatures in the range of 1275°C to 1400°C for a period of time of 5 minutes to 120 minutes. Depending of shape and size of parts to be sintered, other period of sintering time such as 10 minutes to 90 minutes or 15 minutes to 60 minutes may be applied. The sintering atmosphere may be vacuum, inert or reducing such as a hydrogen atmosphere, an atmosphere of a mixture of hydrogen and nitrogen or dissociated ammonia. During the sintering process, the supersaturated elements in ferrite matrix precipitate out as an austenitic phase. Austenite will start precipitating out at the grain boundaries, will grow with further sintering and will precipitate within the grain itself.

[0070] In contrast to other known duplex stainless steel materials, the composition of embodiments of the present invention should not form sigma phases or other hard and deleterious phases, e.g., Chi phase and nitrides, during cooling from an elevated temperature, irrespective of the cooling rate. For example, the amount of sigma phase or other hard and deleterious phases is less than 0.5%. Forced cooling or quenching is thus not necessary to apply. In this context forced cooling means that the sintered parts are subjected to a cooling gas at a pressure above atmospheric pressure. Quenching means that the sintered parts are submerged into a liquid cooling media.

[0071] A microstructure as shown in Figure 1 will typically be formed containing ferrite and austenite. Presence of both phases is responsible for elevated mechanical and corrosion properties. No, or significantly limited amounts of, deleterious phases such as sigma and chi are formed during cooling which are normal for current known duplex stainless steels. As another consequence, this property will reduce or eliminate the formation of such phases during welding where the heat affected zone (HAZ) experience varying cooling rates. In another consequence, this composition will limit the precipitation of such phases during processes such as casting, extrusion, MIM, HIP and additive manufacturing. Embodiments of the invented alloy has shown mechanical and corrosion properties that are comparable to or exceeding the wrought and PM products manufactured with known duplex stainless steel alloys.

[0072] In summary, certain advantages of embodiments of this invention may include fewer tendencies to precipitate deleterious sigma and chi phases that affect the mechanical and corrosion properties. This is particularly of interest in welding. Most of the duplex stainless steel components are welded after they are formed. Welding imparts different cooling rates in different parts of HAZ. These cooling rates tend to precipitate sigma and chi phases along with nitrides due to nitrogen present in the current known alloys. Absence of these phases may eliminate the post heat treatments,

which normally involve annealing at temperatures above 1200°C followed by rapid cooling. This will in most cases become difficult when parts are welded to a bigger structure, limiting use of duplex stainless steel.

FIGURE LEGENDS

5

[0073]

Figure 1 shows the microstructure of invented sintered stainless steel, austenite and ferrite phases are present in equal proportions in as sintered condition, black spots are porosity.

10

Figure 2 discloses a comparison of ultimate tensile strength (UTS) and corrosion properties of the invented sintered stainless steel compared to 300 and 400 alloys, (SAE grades).

15

Figure 3 shows a comparison of mechanical properties of the invented sintered stainless steel at different sintering conditions

EXAMPLES

EXAMPLE 1

20

[0074] A stainless steel powder, having a particle size below 325 mesh, i.e. 95wt% of the particles passed 45 μ m sieve, was mixed with 0.75wt% of Acrawax as a lubricant. The chemical analysis of the stainless steel powder was 0.01wt% C, 1.52wt% Si, 0.2wt% Mn, 0.013wt% P, 0.008wt% S, 24.9wt% Cr, 2.0wt% Cu, 1.3wt% Mo, 1.0wt% W, 0.05wt%N, balance Fe.

25

[0075] The obtained powder mixture was pressed in a uniaxial press and compacted into transverse rupture strength (TRS) bars, according to ASTM B528-16 at a compaction pressure of 750 MPa. The pressed TRS bars were then sintered in 100% hydrogen atmosphere at 1343°C with ramp rate of 7°C/minute for 45 minutes. This was followed by furnace cooling at rate 5°C/minute. The samples were then mounted and polished for microstructure examination. The polished samples were then electro-etched with 33%NaOH at 3V for 15 sec. Electro-etch with NaOH reveals the ferrite phase as tan, austenite as white (unaffected) and sigma phases in dark orange at grain boundaries within ferrite matrix. The microstructure observed is as shown in Figure 1. The microstructure shows approximately 50/50 mixture of ferrite (tan) and austenite (white). There is no sign of any sigma phase (dark orange) in the microstructure. The black spots are porosity in the sample.

30

35

EXAMPLE 2

[0076] Various stainless steel powders according to embodiments of the invention, and as comparative samples, were produced by water atomizing. The chemical composition of the stainless steel powders are shown in table 1. Stainless steel melts having various chemical compositions were melted in an induction furnace, the molten metal was subjected to water stream to obtain steel powder. The obtained powders was then dried and screened to -325 mesh. The screened powder was -45 microns i.e. 95wt% of the powder particles were less than 45 microns. The powders were then mixed with 0.75wt% of the lubricant Acrawax.

40

[0077] In order to test the mechanical properties i.e. ultimate tensile strength (UTS), yield strength (YS) and elongation, TS samples (dog bone) per ASTM B925-15 were pressed with a compaction pressure of 750 MPa. The bars were then sintered as mentioned in Example 1. The sintered bars were then tested for mechanical properties per ASTM E8/E8M-16a. Metallographic examination was also conducted in order to establish the ratio between austenite and ferrite in sintered samples. The test results are shown in table 2 in comparison with published data from samples of known duplex stainless steels in wrought, (DSS 329 Wrought), and gas atomized and hiped conditions (DSS 329 PM GA).

45

[0078] Table 2 shows that the stainless steel powders according to the present invention can be used for producing sintered duplex stainless steel having desired mechanical properties.

50

55

Table 1, chemical compositions of various stainless steel powders, there production method and type of process for producing sintered samples.

Chemical analysis [% by weight]														
Sample	Type	C	Si	Mn	S	P	Cr	Ni	Mo	W	Cu	O	N	Other
Comparative	DSS 329 Wrought	0.08		1.00			23-28	2.5-5	1-2				0.08	
Comparative	DSS 329 PM WA	0.20	0.75	1.00			23-28	2.5-5	1-2			0.05	0.08	
Comparative	DSS 2205 PM GA	0.03	1.00	2.00	0.020	0.030	22.0-23.0	4.5-6.5	3.0-3.5		0.75		0.14-0.20	
Premix	XSSDP1 PM WA Premix	0.03	2.00	0.10	0.006	0.008	25	5.5	1.3	1	2	0.2	0.06	
Invention	XSSDP1 PM WA Prealloy	0.01	1.52	0.20	0.013	0.008	24.9	5.5	1.3	1	2	0.15	0.05	
Invention	XSS DP1-1	0.03	1.97	0.10	0.007	0.012	23.4	5.1	1.2	0.9	1.9	0.13	0.05	
Invention	XSS DP1-2	0.03	2.12	0.20	0.007	0.012	26.1	5.2	1.3	0.9	3	0.15	0.02	

5
10
15
20
25
30
35
40
45
50
55

(continued)

Chemical analysis [% by weight]															
	Sample	Type	C	Si	Mn	S	P	Cr	Ni	Mo	W	Cu	O	N	Other
Invention	XSS DP1-3	Water atomized powder, prealloyed compacted and sintered	0.03	1.94	0.20	0.008	0.013	25.1	5.6	1.2	0.8	2	0.15	0.02	0.58 Nb
Comparative	XSS DP1-4	Water atomized powder, prealloyed compacted and sintered	0.03	2.14	0.20	0.009	0.015	22.3	5.2	1.3	0.9	1.9	0.16	0.06	0.6 Sn
4 Premix of 316L, 434L and elemental powders of Si, W and Cu.															

EP 3 551 775 B1

Table 2, mechanical properties and metallographic structure for sintered samples produced from stainless steel powders according to table 1.

Mechanical Properties									
	Sample	Type	Sintering time [minutes]	TS [Mpa]	YS [Mpa]	TRS [Mpa]	Elongation [%]	% austenite in ferrite matrix	
5									
10	Comparative	DSS 329 Wrought	Annealed	725	550		25	-50	
	Comparative	DSS 329 PM WA	Water atomized powder, HIP	45	523	460	180	7	0
15	Comparative	DSS 2205 PM GA	Gas atomized powder, HIP	45	578	427	200	11	-50
20	Comparative	XSS DP1 PM WA Premix	Water atomized powders ⁵ , compacted and sintered	45	720	700	220	2.5	-35
25	Invention	XSS DP1 PM WA Prealloy	Water atomized powder, prealloyed compacted and sintered	45	776	617	278	8.6	-60
30	Invention	XSS DP1-1	Water atomized powder, prealloyed compacted and sintered	45	727	504	275	11.0	~ 50
35	Invention	XSS DP1-2	Water atomized powder, prealloyed compacted and sintered	45	809	745	265	2.5	-50
40	Invention	XSS DP1-3	Water atomized powder, prealloyed compacted and sintered	45	843	691	257	6.5	-45
45	Comparative	XSS DP1-4	Water atomized powder, prealloyed compacted and sintered	45	749	743	218	0.5	-10
50	⁵ Premix of 316L, 434L and elemental powders of Si, W and Cu.								

[0079] An embodiment of the invented powder with composition as in Example 1 was also sintered at various temperatures and atmospheres below, to show the effect on mechanical properties. Such data is plotted in Figure 3.

55

- A. 2500°F for 45 minutes in hydrogen gas
- B. 2450°F for 45 minutes in hydrogen gas
- C. 2450°F for 60 minutes in hydrogen gas

- D. 2300°F for 60 minutes in hydrogen gas
- E. 2250°F for 60 minutes in hydrogen gas
- F. 2250°F for 60 minutes in dissociated ammonia

5 EXAMPLE 3

[0080] In order to perform corrosion test, TRS bars as in Example 1 were produced along with bars for 316L and 434L as representatives from austenitic and ferritic grades. The samples were then tested for corrosion in 5% NaCl solution at room temperature per ASTM B895-16. The corrosion was compared by the hours takes for onset of corrosion on the samples. The comparative data is plotted in Figure 2 along with the UTS and YS for these samples. The diameter of the bubbles in the Figure 3 represents the number of hours taken for the start of the corrosion on the samples. The corrosion test for the invented powder was discontinued after 3700 hours as there was no sign of corrosion and it already exceeded 3 times that of 316L samples.

15

Claims

1. A stainless steel powder comprising in weight %:

20 up to 0.1% of C,
 0.5-3% of Si,
 up to 0.5% of Mn,
 20-27% of Cr,
 3-8% of Ni,
 25 1-6% of Mo,
 up to 3% of W,
 up to 0.1% N,
 up to 4% of Cu,
 up to 0.04% of P,
 30 up to 0.04% of S,
 unavoidable impurities up to 0.8% whereof Sn may be present up to 0.2%, optionally one or more of up to 0.004% B, up to 1% Nb, up to 0.5% Hf, up to 1% Ti, up to 1% Co,
 rest Fe.

35 2. A stainless steel powder according to claim 1 comprising in weight %:

up to 0.06% of C,
 1-3% of Si,
 up to 0.3% of Mn,
 40 23-27% of Cr,
 4-7% of Ni,
 1-3% of Mo,
 0.8-1.5% of W,
 up to 0.07% N,
 45 1-3% of Cu,
 up to 0.03% of P,
 up to 0.03% of S,
 unavoidable impurities up to 0.8% whereof Sn may be present up to 0.2%, optionally one or more of up to 0.004% B, up to 1% Nb, up to 0.5% Hf, up to 1% Ti, up to 1% Co,
 50 rest Fe.

3. A stainless steel powder according to claim 1 comprising in weight %:

55 up to 0.03% of C,
 1.5-2.5% of Si,
 up to 0.3% of Mn,
 24-26% of Cr,
 5-7% of Ni,

1-1.5% of Mo,
 1-1.5% of W,
 up to 0.06% N,
 1-3% of Cu,
 up to 0.02% of P,
 up to 0.015% of S,
 unavoidable impurities up to 0.8% whereof Sn may be present up to 0.2%, optionally one or more of up to 0.004% B, up to 1% Nb, up to 0.5% Hf, up to 1% Ti, up to 1% Co,
 rest Fe.

4. A stainless steel powder according to any of claims 1 to 3 wherein the stainless steel powder is ferritic.
5. A stainless steel powder according to any of claims 1 to 4 wherein the stainless steel powder is produced by water atomization.
6. A stainless steel powder according to any of claims 1 to 4 wherein the stainless steel powder is produced by gas atomization.
7. A stainless steel powder according to any of claims 1 to 4 wherein the particle size of the powder is between 53 microns and 18 microns such that at least 80% of the particles are less than 53 microns and at most 20% of the particles are less than 18 microns measured by laser diffraction according to ISO 13320:1999.
8. A stainless steel powder according to any of claims 1 to 4 wherein the particle size of the powder is between 26 microns and 5 microns such that at least 80% of the particles are less than 26 microns and at most 20% of the particles are less than 5 microns measured by laser diffraction according to ISO 13320:1999.
9. A stainless steel powder according to any of claims 1 to 4 wherein the particle size of the powder is between 150 microns and 26 microns such that at least 80% of the particles are less than 150 microns and at most 20% of the particles are less than 26 microns measured by laser diffraction according to ISO 13320:1999.
10. A stainless steel powder according to any of claims 1 to 4 wherein the powder is a prealloyed powder.
11. A method for producing a stainless steel powder by water atomization comprising the steps of:
- providing a molten metal of having a chemical composition corresponding to the chemical composition of the stainless steel powder according to claim 1,
 - subjecting a stream of the molten metal to water atomization,
 - recovery of the obtained stainless steel powder.
12. A sintered duplex stainless steel having a chemical composition according to any of claims 1-3 and wherein the microstructure of the sintered duplex stainless steel is **characterized by** austenite phase precipitated in ferrite phase.
13. A sintered duplex stainless steel according to claim 12 wherein the Ni equivalent (Ni_{eq}) is such that $5 < Ni_{eq} < 11$ and the Cr equivalent (Cr_{eq}) is such that $27 < Cr_{eq} < 38$ and wherein Cr_{eq} and Ni_{eq} are calculated according to the formulas:

$$Cr_{eq} = Cr + 2Si + 1.5Mo + 0.75W$$

$$Ni_{eq} = Ni + 0.5Mn + 0.3Cu + 25N + 30C$$

and,

wherein Cr, Ni, etc. are the level of each element in the alloy in weight %.

14. A sintered duplex stainless steel according to any of claims 12 to 13 wherein the pitting resistance equivalent number

EP 3 551 775 B1

(PREN) is $28 < \text{PREN} < 33$ and wherein PREN is calculated according to the formula:

$$\text{PREN} = \text{Cr} + 3.3\text{Mo} + 16\text{N}$$

5

and,

wherein Cr, Mo and N are the level of each element in the alloy in weight % .

10

15. A sintered duplex stainless steel according to claim 12 wherein the microstructure of the sintered duplex stainless steel contains 30-70% austenite.

16. A sintered duplex stainless steel according to any of claims 12 to 15 wherein the microstructure is **characterized by** being free from sigma phases and nitrides.

15

17. A method for producing the duplex sintered stainless steel of claim 12 comprising the steps of:

20

- providing a stainless steel powder according to according to any of claims 1 to 10,
- optionally mixing the stainless steel powder with a lubricant and optionally other additives,
- subjecting the stainless steel powder or the mixture to a consolidation process forming a green component,
- subjecting the compacted green component to a sintering step in an inert or reducing atmosphere or in vacuum at a temperature between 1150 °C to 1450 °C, preferably at a temperature between 1275 °C to 1400 °C for a period of time of 5 minutes to 120 minutes ,
- subjecting the sintered component to a cooling step down to ambient temperature.

25

18. A method for producing a duplex sintered stainless according to claim 17 wherein the consolidation process includes:

- uniaxial compaction at a compaction pressure of up to 900 MPa in a die to form a green component,
- ejecting the obtained compacted green component from the die.

30

Patentansprüche

1. Edelstahlpulver, umfassend in Gew.-%:

35

bis zu 0,1 % C,
0,5-3 % Si,
bis zu 0,5 % Mn,
20-27 % Cr,
3-8 % Ni,
1-6 % Mo,
bis zu 3 % W,
bis zu 0,1 % N,
bis zu 4 % Cu,
bis zu 0,04 % P,
bis zu 0,04 % S,
unvermeidbare Verunreinigungen bis zu 0,8 %, wovon Sn bis zu 0,2 % vorhanden sein kann, gegebenenfalls eines oder mehrere von bis zu 0,004 % B, bis zu 1 % Nb, bis zu 0,5 % Hf, bis zu 1 % Ti, bis zu 1 % Co,
Rest Fe.

40

45

50

2. Edelstahlpulver nach Anspruch 1, umfassend in Gew.-%:

55

bis zu 0,06 % C,
1-3 % Si,
bis zu 0,3 % Mn,
23-27 % Cr,
4-7 % Ni,
1-3 % Mo,
0,8-1,5 % W,

EP 3 551 775 B1

bis zu 0,07 % N,
1-3 % Cu,
bis zu 0,03 % P,
bis zu 0,03 % S,

5 unvermeidbare Verunreinigungen bis zu 0,8 %, wovon Sn bis zu 0,2 % vorhanden sein kann, gegebenenfalls eines oder mehrere von bis zu 0,004 % B, bis zu 1 % Nb, bis zu 0,5 % Hf, bis zu 1 % Ti, bis zu 1 % Co, Rest Fe.

3. Edelstahlpulver nach Anspruch 1, umfassend in Gew.-%:

10 bis zu 0,03 % C,
1,5-2,5 % Si,
bis zu 0,3 % Mn,
24-26 % Cr,
15 5-7 % Ni,
1-1,5 % Mo,
1-1,5 % W,
bis zu 0,06 % N,
1-3 % Cu,
20 bis zu 0,02 % P,
bis zu 0,015 % S,
unvermeidbare Verunreinigungen bis zu 0,8 %, wovon Sn bis zu 0,2 % vorhanden sein kann, gegebenenfalls
eines oder mehrere von bis zu 0,004 % B, bis zu 1 % Nb, bis zu 0,5 % Hf, bis zu 1 % Ti, bis zu 1 % Co,
Rest Fe.

4. Edelstahlpulver nach einem der Ansprüche 1 bis 3, wobei das Edelstahlpulver ferritisch ist.

5. Edelstahlpulver nach einem der Ansprüche 1 bis 4, wobei das Edelstahlpulver durch Wasserzerstäubung hergestellt wird.

6. Edelstahlpulver nach einem der Ansprüche 1 bis 4, wobei das Edelstahlpulver durch Gaszerstäubung hergestellt wird.

7. Edelstahlpulver nach einem der Ansprüche 1 bis 4, wobei die Teilchengröße des Pulvers zwischen 53 Mikrometer und 18 Mikrometer liegt, sodass mindestens 80 % der Teilchen kleiner als 53 Mikrometer sind und höchstens 20 % der Teilchen kleiner als 18 Mikrometer sind, gemessen durch Laserbeugung gemäß ISO 13320:1999.

8. Edelstahlpulver nach einem der Ansprüche 1 bis 4, wobei die Teilchengröße des Pulvers zwischen 26 Mikrometer und 5 Mikrometer liegt, sodass mindestens 80 % der Teilchen kleiner als 26 Mikrometer sind und höchstens 20 % der Teilchen kleiner als 5 Mikrometer sind, gemessen durch Laserbeugung gemäß ISO 13320:1999.

9. Edelstahlpulver nach einem der Ansprüche 1 bis 4, wobei die Teilchengröße des Pulvers zwischen 150 Mikrometer und 26 Mikrometer liegt, sodass mindestens 80 % der Teilchen kleiner als 150 Mikrometer sind und höchstens 20 % der Teilchen kleiner als 26 Mikrometer sind, gemessen durch Laserbeugung gemäß ISO 13320:1999.

10. Edelstahlpulver nach einem der Ansprüche 1 bis 4, wobei das Pulver ein vorlegiertes Pulver ist.

11. Verfahren zur Herstellung eines Edelstahlpulvers durch Wasserzerstäubung, umfassend die Schritte:

- Bereitstellen eines geschmolzenen Metalls mit einer chemischen Zusammensetzung, die der chemischen Zusammensetzung des Edelstahlpulvers nach Anspruch 1 entspricht,
- Unterziehen eines Stroms des geschmolzenen Metalls einer Wasserzerstäubung,
- Rückgewinnung des erhaltenen Edelstahlpulvers.

12. Gesinterter Duplexedelstahl mit einer chemischen Zusammensetzung nach einem der Ansprüche 1 bis 3 und wobei die Mikrostruktur des gesinteren Duplexedelstahls **durch** eine in der Ferritphase ausgeschiedene Austenitphase **gekennzeichnet ist**.

EP 3 551 775 B1

13. Gesinterter Duplexedelstahl nach Anspruch 12, wobei das Ni-Äquivalent (Ni_{eq}) so beschaffen ist, dass $5 < Ni_{eq} < 11$ und das Cr-Äquivalent (Cr_{eq}) so beschaffen ist, dass $27 < Cr_{eq} < 38$ und wobei Cr_{eq} und Ni_{eq} gemäß den folgenden Formeln berechnet werden:

$$Cr_{eq} = Cr + 2Si + 1,5Mo + 0,75W$$

$$Ni_{eq} = Ni + 0,5Mn + 0,3Cu + 25N + 30C$$

und, wobei Cr, Ni usw. der Gehalt eines jeden Elements in der Legierung in Gew.-% sind.

14. Gesinterter Duplexedelstahl nach einem der Ansprüche 12 bis 13, wobei die Lochfraßwiderstandsäquivalenzzahl (PREN) $28 < PREN < 33$ beträgt und wobei PREN gemäß der folgenden Formel berechnet wird:

$$PREN = Cr + 3,3Mo + 16N$$

und, wobei Cr, Mo und N der Gehalt eines jeden Elements in der Legierung in Gew.-% sind.

15. Gesinterter Duplexedelstahl nach Anspruch 12, wobei die Mikrostruktur des gesinterten Duplexedelstahls 30-70 % Austenit enthält.

16. Gesinterter Duplexedelstahl nach einem der Ansprüche 12 bis 15, wobei die Mikrostruktur **dadurch gekennzeichnet ist, dass** sie frei von Sigma-Phasen und Nitriden ist.

17. Verfahren zur Herstellung des gesinterten Duplexedelstahls nach Anspruch 12, umfassend die Schritte:

- Bereitstellen eines Edelstahlpulvers nach einem der Ansprüche 1 bis 10,
- gegebenenfalls Mischen des Edelstahlpulvers mit einem Schmiermittel und gegebenenfalls anderen Zusatzstoffen,
- Aussetzen des Edelstahlpulvers oder der Mischung gegenüber einem Verfestigungsprozess, wodurch eine Grünkomponente gebildet wird,
- Aussetzen der verfestigten Grünkomponente gegenüber einem Sinterschritt in einer inerten oder reduzierenden Atmosphäre oder im Vakuum bei einer Temperatur zwischen 1150 °C bis 1450 °C, vorzugsweise bei einer Temperatur zwischen 1275 °C bis 1400 °C für einen Zeitraum von 5 Minuten bis 120 Minuten,
- Unterziehen der gesinterten Komponente einem Abkühlungsschritt bis auf Umgebungstemperatur.

18. Verfahren zur Herstellung eines gesinterten Duplexedelstahls nach Anspruch 17, wobei der Verfestigungsprozess einschließt:

- uniaxiales Verdichten bei einem Verdichtungsdruck von bis zu 900 MPa in einer Matrize, um eine Grünkomponente zu bilden,
- Auswerfen der erhaltenen verdichteten Grünkomponente aus der Matrize.

Revendications

1. Poudre d'acier inoxydable comprenant en % en poids :

jusqu'à 0,1 % de C,
0,5 à 3 % de Si,
jusqu'à 0,5 % de Mn,
20 à 27 % de Cr,
3 à 8 % de Ni,
1 à 6 % de Mo,

EP 3 551 775 B1

jusqu'à 3 % de W,
jusqu'à 0,1 % de N,
jusqu'à 4 % de Cu,
jusqu'à 0,04 % de P,
jusqu'à 0,04 % de S,
des impuretés inévitables jusqu'à 0,8 % dont Sn peut être présent jusqu'à 0,2 %, facultativement un ou plusieurs
parmi jusqu'à 0,004 % de B, jusqu'à 1 % de Nb, jusqu'à 0,5 % de Hf, jusqu'à 1 % de Ti, jusqu'à 1 % de Co,
le reste de Fe.

2. Poudre d'acier inoxydable selon la revendication 1 comprenant en % en poids :

jusqu'à 0,06 % de C,
1 à 3 % de Si,
jusqu'à 0,3 % de Mn,
23 à 27 % de Cr,
4 à 7 % de Ni,
1 à 3 % de Mo,
0,8 à 1,5 % de W,
jusqu'à 0,07 % de N,
1 à 3 % de Cu,
jusqu'à 0,03 % de P,
jusqu'à 0,03 % de S,
des impuretés inévitables jusqu'à 0,8 % dont Sn peut être présent jusqu'à 0,2 %, facultativement un ou plusieurs
parmi jusqu'à 0,004 % de B, jusqu'à 1 % de Nb, jusqu'à 0,5 % de Hf, jusqu'à 1 % de Ti, jusqu'à 1 % de Co,
le reste de Fe.

3. Poudre d'acier inoxydable selon la revendication 1 comprenant en % en poids :

jusqu'à 0,03 % de C,
1,5 à 2,5 % de Si,
jusqu'à 0,3 % de Mn,
24 à 26 % de Cr,
5 à 7 % de Ni,
1 à 1,5 % de Mo,
1 à 1,5 % de W,
jusqu'à 0,06 % de N,
1 à 3 % de Cu,
jusqu'à 0,02 % de P,
jusqu'à 0,015 % de S,
des impuretés inévitables jusqu'à 0,8 % dont Sn peut être présent jusqu'à 0,2 %, facultativement un ou plusieurs
parmi jusqu'à 0,004 % de B, jusqu'à 1 % de Nb, jusqu'à 0,5 % de Hf, jusqu'à 1 % de Ti, jusqu'à 1 % de Co,
le reste de Fe.

4. Poudre d'acier inoxydable selon l'une quelconque des revendications 1 à 3 dans laquelle la poudre d'acier inoxydable est ferritique.

5. Poudre d'acier inoxydable selon l'une quelconque des revendications 1 à 4 dans laquelle la poudre d'acier inoxydable est produite par atomisation aqueuse.

6. Poudre d'acier inoxydable selon l'une quelconque des revendications 1 à 4 dans laquelle la poudre d'acier inoxydable est produite par atomisation gazeuse.

7. Poudre d'acier inoxydable selon l'une quelconque des revendications 1 à 4 dans laquelle la taille de particules de la poudre est comprise entre 53 micromètres et 18 micromètres de telle sorte qu'au moins 80 % des particules sont inférieures à 53 micromètres et au plus 20 % des particules sont inférieures à 18 micromètres mesuré par diffraction laser selon ISO 13320:1999.

8. Poudre d'acier inoxydable selon l'une quelconque des revendications 1 à 4 dans laquelle la taille de particules de

EP 3 551 775 B1

la poudre est comprise entre 26 micromètres et 5 micromètres de telle sorte qu'au moins 80 % des particules sont inférieures à 26 micromètres et au plus 20 % des particules sont inférieures à 5 micromètres mesuré par diffraction laser selon ISO 13320:1999.

- 5 9. Poudre d'acier inoxydable selon l'une quelconque des revendications 1 à 4 dans laquelle la taille de particules de la poudre est comprise entre 150 micromètres et 26 micromètres de telle sorte qu'au moins 80 % des particules sont inférieures à 150 micromètres et au plus 20 % des particules sont inférieures à 26 micromètres mesuré par diffraction laser selon ISO 13320:1999.
- 10 10. Poudre d'acier inoxydable selon l'une quelconque des revendications 1 à 4 dans laquelle la poudre est une poudre préalliée.
11. Procédé de production d'une poudre d'acier inoxydable par atomisation aqueuse comprenant les étapes consistant à :
- 15
- fournir un métal fondu ayant une composition chimique correspondant à la composition chimique de la poudre d'acier inoxydable selon la revendication 1,
 - soumettre un courant du métal fondu à une atomisation aqueuse,
 - récupérer la poudre d'acier inoxydable obtenue.
- 20
12. Acier inoxydable duplex fritté ayant une composition chimique selon l'une quelconque des revendications 1 à 3 et dans lequel la microstructure de l'acier inoxydable duplex fritté est **caractérisée par** une phase austénite précipitée dans une phase ferrite.
- 25 13. Acier inoxydable duplex fritté selon la revendication 12 dans lequel l'équivalent Ni ($Ni_{\text{éq}}$) est tel que $5 < Ni_{\text{éq}} < 11$ et l'équivalent Cr ($Cr_{\text{éq}}$) est tel que $27 < Cr_{\text{éq}} < 38$ et dans lequel $Cr_{\text{éq}}$ et $Ni_{\text{éq}}$ sont calculés selon les formules :

$$Cr_{\text{éq}} = Cr + 2Si + 1,5Mo + 0,75W$$

$$Ni_{\text{éq}} = Ni + 0,5Mn + 0,3Cu + 25N + 30C$$

et, dans lequel Cr, Ni, etc. sont le taux de chaque élément dans l'alliage en % en poids.

14. Acier inoxydable duplex fritté selon l'une quelconque des revendications 12 à 13 dans lequel le nombre équivalent de résistance aux piqûres (PREN) est $28 < PREN < 33$ et dans lequel PREN est calculé selon la formule :

$$PREN = Cr + 3,3Mo + 16N$$

et, dans lequel Cr, Mo et N sont le taux de chaque élément dans l'alliage en % en poids.

15. Acier inoxydable duplex fritté selon la revendication 12 dans lequel la microstructure de l'acier inoxydable duplex fritté contient 30 à 70 % d'austénite.
16. Acier inoxydable duplex fritté selon l'une quelconque des revendications 12 à 15 dans lequel la microstructure est **caractérisée en ce qu'elle** est exempte de phases sigma et de nitrures.
17. Procédé de production de l'acier inoxydable fritté duplex de la revendication 12 comprenant les étapes consistant à :
- fournir une poudre d'acier inoxydable selon l'une quelconque des revendications 1 à 10,
 - facultativement mélanger la poudre d'acier inoxydable avec un lubrifiant et facultativement d'autres additifs,
 - soumettre la poudre d'acier inoxydable ou le mélange à un processus de consolidation formant un composant vert,
 - soumettre le composant vert compacté à une étape de frittage dans une atmosphère inerte ou réductrice ou

EP 3 551 775 B1

sous vide à une température comprise entre 1150 °C et 1450 °C, de préférence à une température comprise entre 1275 °C et 1400 °C pendant une période de temps de 5 minutes à 120 minutes,
- soumettre le composant fritté à une étape de refroidissement jusqu'à température ambiante.

5 **18.** Procédé de production d'un inoxydable fritté duplex selon la revendication 17 dans lequel le processus de consolidation inclut :

10 - un compactage uniaxial à une pression de compactage allant jusqu'à 900 MPa dans une matrice pour former un composant vert,
- l'éjection du composant vert compacté obtenu de la matrice.

15

20

25

30

35

40

45

50

55

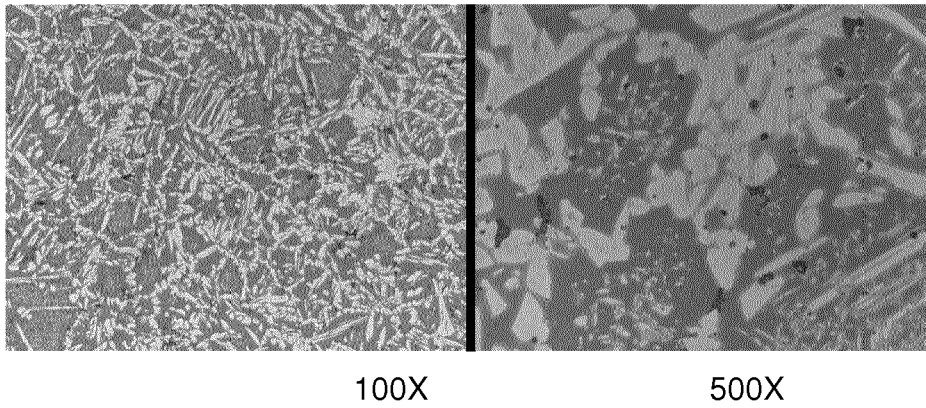


Figure 1: Microstructure of invented alloy shows austenite and ferrite phases in equal proportions in as sintered condition, black spots are porosity.

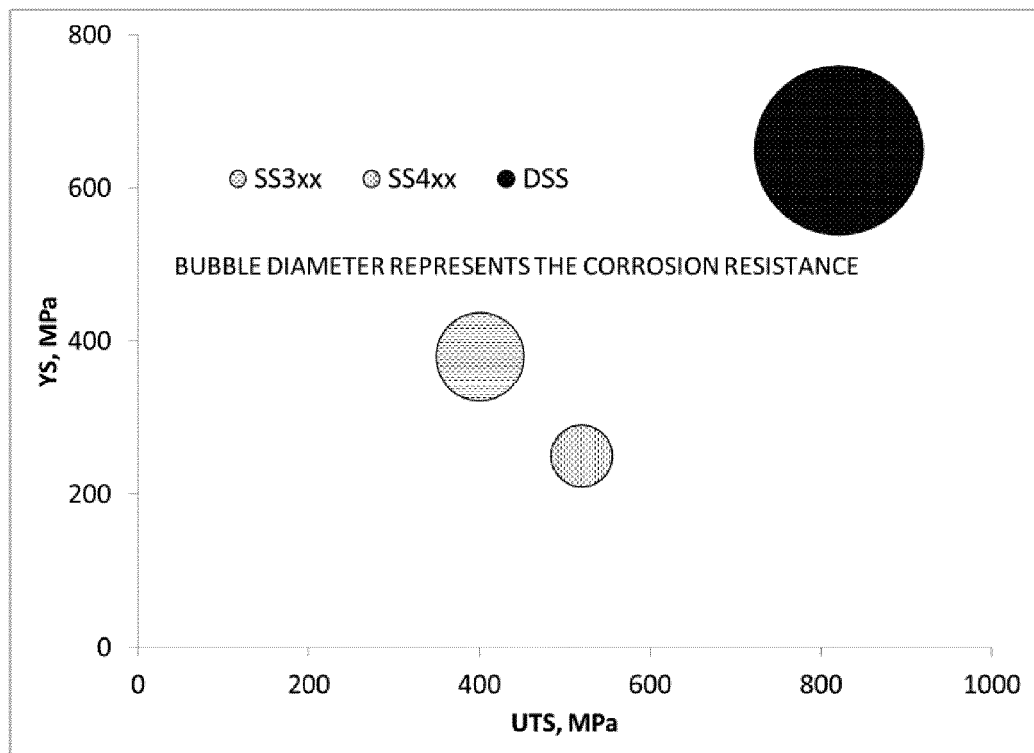


Figure 2: Comparison of UTS and Corrosion Properties of invented alloy to 300 and 400 alloys

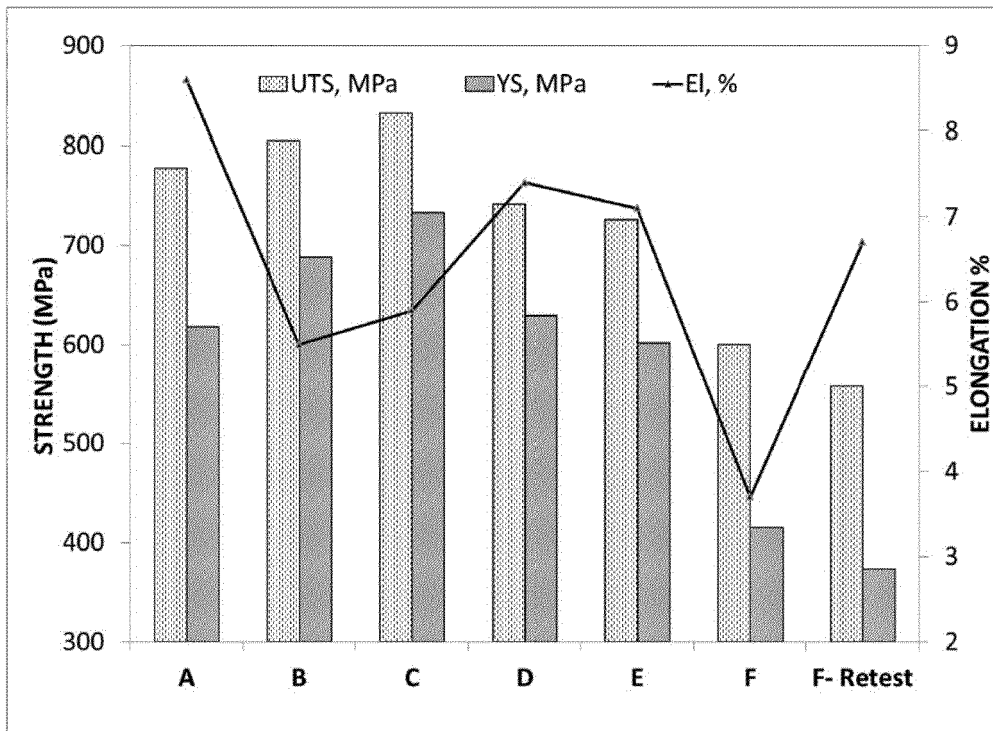


Figure 3: Comparison of Mechanical Properties of invented alloy at different sintering conditions

REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- EP 0167822 A1 [0012]
- JP 5263199 A [0013]
- EP 0534864 B1 [0014]

Non-patent literature cited in the description

- **A. LAWLEY ; E. WAGNER ; C.T. SCHADE.** *Advances in Powder Metallurgy and Particulate Materials*, 2005, 78-89 [0008]
- **L.A. DOBRZANSKI ; Z. BRYTAN ; M. ACTIS GRANDE ; M. ROSSO.** *Archives of Materials Science and Engineering*, April 2007, vol. 28 (4), 217-223 [0008]
- **L.A. DOBRZANSKI ; Z. BRYTAN ; M. ACTIS GRANDE ; M. ROSSO.** *Journal of Achievements in Materials and Manufacturing Engineering*, vol. 17 (1-2), 317-320 [0008]