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# Powder-based additive manufacturing of high-nitrogen stainless steels and austenitic nickel alloys

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(54) Title: POWDER-BASED ADDITIVE MANUFACTURING OF HIGH-NITROGEN STAINLESS STEELS AND AUSTENITIC NICKEL ALLOYS
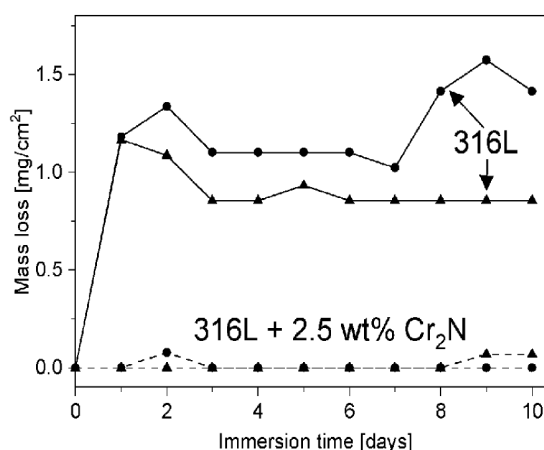


FIGURE 4

(57) **Abstract**: Powder mixture compositions, consisting essentially of a stainless steel or austenitic nickel alloy powder and an additive powder containing chromium and nitrogen and/or carbon, are disclosed, together with the use of such powder mixture compositions in full-melt powder-based additive manufacturing to build components having increased levels of dissolved chromium and nitrogen, and/ or carbon, leading to improved mechanical properties and corrosion resistance.

TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

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POWDER-BASED ADDITIVE MANUFACTURING OF HIGH-NITROGEN STAINLESS STEELS AND
AUSTENITIC NICKEL ALLOYS

FIELD OF THE INVENTION

5  The invention relates to additive manufacturing of alloys and, more particularly, to powder-based
additive manufacturing of stainless steels and austenitic nickel alloys.

BACKGROUND OF THE INVENTION

Steels containing high levels of dissolved nitrogen—more than can be retained in molten iron at
atmospheric pressure—show improvements across a range of properties, from increased hardness,

10  strength, and ductility to superior corrosion resistance. Such high-nitrogen steels, particularly
stainless steels, have been produced in bulk using a range of processing techniques, from high
nitrogen partial pressure melting to alloying the melt with elements that increase nitrogen solubility,
such as Cr, Mn and Mo. J.W. Simmons, Mat. Sci. & Eng., Vol. A207 (1996) 159, 160; G. Stein & I.
Hucklenbroich, Mat. & Manuf. Proc., Vol. 19, No. 1 (2004) 7, 8-10. Similar increases in corrosion

15  resistance, hardness, strength and ductility arising from high levels of dissolved nitrogen have also
been identified for nickel-chromium-iron-alloys having an austenitic face centered cubic ("FCC")
structure. H.J.C. Speidel & M.O. Speidel, Mat. & Manuf. Proc., Vol. 19, No. 1 (2004) 95–109.

Stainless steel or other alloy components can be formed by additive manufacturing ("AM"), using
stainless steel or other alloy powder and a directed heat source, typically a laser or electron beam. In

20  full-melt powder-based AM, selected regions of the relevant powder are melted and solidified, as
opposed to simply heated and fused, to successively build up, or print, a three-dimensional
component. In Powder Bed Fusion ("PBF") systems, referred to as L-PBF when used with a laser
source, the selected regions of heated powder are located within a succession of powder layers
formed sequentially in a powder bed. In Directed Energy Deposition (DED) systems, the selected

25  regions of heated powder are located where the powder is delivered through a nozzle onto a
substrate.

As a consequence of the additional processing steps—powder formation, melting and
solidification—as-built stainless steel and other alloy components formed by full-melt powder-based
AM do not necessarily exhibit the same composition, microstructure and properties as the bulk

30  material from which the powder was produced, which can be both an advantage and disadvantage.

Efforts have been made to increase and control nitrogen content, including the dissolved nitrogen
content, of stainless steel components formed by full-melt powder-based AM.

E.H. Valente, T. L. Christiansen and M.A.J. Somers, ESSC & DUPLEX 2019 (2019) 42-51 investigated the introduction of nitrogen into the surfaces of components built using full melt L-PBF from AISI 316L austenitic stainless steel powder. In particular, Valente et al. investigated the effects of heat treatment and low and high temperature gaseous surface nitriding on the microstructure, wear characteristics, corrosion resistance and surface composition of such components.

Published Chinese patent application CN 108941563A (Univ. Southern Sci. & Tech.) reports nitrogen-induced pore formation in full-melt L-PBF-built martensitic steel components. In particular, CN 108941563A reports L-PBF production of air-permeable, having more than 20 % porosity, mold steel from a powder mixture composed of 15-65 µm diameter spherical S136 steel (Fe Bal.; C 0.38; Si 0.8; Mn 0.5; Cr 13.6; P <0.03; S <0.03) mixed with 5 to 10 wt% of 10 µm diameter chromium nitride (CN).

Published international patent application WO 2020/221689 (Deutsche Edelstahlwerke Specialty Steel & Co KG) refers to the use of L-PBF and heat treatment for the formation of high hardness martensitic stainless steel components containing nitride inclusions. WO 2020/221689 indicates use of L-PBF processing, optionally under a nitrogen atmosphere, of steel powder containing: 0.5 to 5 or 6 wt% C or N; 0.1 - 2.5 wt% of Si or Mn; at least one carbide or nitride forming metal in the proportion Cr: 5 – 25 wt%, Mo: 0.5 – 15 wt%, V: 0.5 – 15 wt%, Ti: 0.5 – 5 wt%, Nb: 0.5 – 15 wt%, or W: 0.5 - 15 wt%, and, optionally, an unspecified amount of an unspecified-metal nitride powder. WO 2020/221689 describes formation of L-PBF built components, containing 25 to 85 vol.% austenitic steel, and, after heat treatment, up to 80 vol.% martensitic steel and 5-50 vol.% of "hard phase" carbide/nitride particles of unspecified composition.

It would be advantageous to increase the dissolved nitrogen, and/or dissolved carbon, content of full-melt powder-based AM-built stainless steel and austenitic nickel alloy components and so improve the wear, corrosion resistance, hardness and other properties of such components.

OBJECT OF THE INVENTION

It is an object of the present invention to provide powder mixture compositions for use in full-melt additive manufacturing of stainless steel and austenitic nickel alloys containing high levels of dissolved nitrogen and having improved properties.

It is another object of the present invention to avoid the above-mentioned disadvantages of the above mentioned methods for additively manufacturing stainless steel and austenitic nickel alloy components.

It is a further object of the invention to provide an alternative to the prior art.

SUMMARY OF THE INVENTION

Thus, the above-described objects and several other objects are intended to be obtained in a first aspect of the invention by providing a powder mixture composition consisting essentially of up to 20 weight percent of an additive powder substantially comprising a chromium nitride powder and, optionally, chromium powder, wherein, by weight percent of the additive powder, the Cr:N ratio is

5 greater than 4, and balance of an alloy powder substantially comprising Fe, Cr, and Ni, and optionally Mo and Mn, wherein, by weight percent of the powder mixture composition, the powder mixture substantially comprises N no more than 5 and: Cr from 10.5 to 35, Ni up to 38, Mo up to 10 and Mn up to 19, and balance Fe; or Cr from 0.5 to 50, Fe up to 40, Mo 0 to 30, Mn 0 to 3 and balance Ni.

Consisting essentially of means that specific further components not materially affecting the

10 essential characteristics of the powder mixture composition may be, but need not be, present. An essential characteristic of the powder mixture composition is its suitability for use in full-melt additive manufacturing using the methods specified herein to build alloy components having the compositions and properties specified herein.

Substantially comprising or comprises means that specific further components not materially

15 affecting the essential characteristics of the additive powder or alloy powder may be, but need not be, present. An essential characteristic of the additive powder and the alloy powder is their suitability for use in full-melt additive manufacturing using the methods specified herein to build alloy components having the compositions and properties specified herein.

A powder means a material composed of particles that are sufficiently small and sufficiently

20 disinclined to aggregate to allow the powder to flow through a nozzle or similar opening and be distributed in a flat and uniform layer in a powder bed or by directed onto an area of a substrate. For present purposes, typical powder sizes may be between 1 and 500 μm, preferably between 10 μm and 50 μm for PBF and 50 μm and 150 μm for DED. Nitrides and carbides and single element powders such as Mo, Mn, Cr and C, taking into account the different size constraints for PBF and

25 DED, can be any range from a few nanometers to around 150 μm.

A powder mixture means an additive powder and alloy powder that have been mixed together, using a known or yet to be developed powder mixing technique.

A powder mixture composition means a powder mixture having a certain chemical composition or range of chemical compositions, a fraction of the powder mixture composition being due to an

30 additive powder, having a certain chemical composition or range of chemical compositions, and the remaining fraction of the powder mixture composition being due to an alloy powder, having a certain chemical composition or range of chemical compositions.

An additive powder means a powder formed from a single additive material, having a certain chemical composition or range of chemical compositions, or more than one powder, each formed from an additive material, each having a certain chemical composition or range of chemical compositions.

5 Chromium nitride means chromium mono-nitride or di-chromium nitride or any stoichiometric or non-stoichiometric compound of chromium and nitrogen.

A chromium nitride or chromium powder means a powder consisting of chromium nitride or chromium and unavoidable trace elements, including molecules reacting with or adhering to the surface of the powder particles.

10 An advantage of a powder mixture composition substantially comprising up to 20 wt% of a chromium nitride powder, and optionally a chromium powder, is the ability it offers to independently control the nitrogen content of the powder mixture composition up to 5 wt % N, and thus the nitrogen content, including dissolved nitrogen content, of an alloy component built by full-melt AM from the powder mixture composition, leading to improved mechanical properties and

15 corrosion resistance of the alloy component.

An advantage of a powder mixture consisting essentially of up to 20 wt% of a chromium nitride powder, and optionally a chromium powder, and balance of an alloy powder, is the ability it confers to largely independently control the nitrogen and chromium content of the powder mixture composition, and the dissolved nitrogen and chromium content of an alloy component built by full-

20 melt AM from the powder mixture composition. An advantage of having a Cr:N ratio greater than 4 is its tendency to suppress, over a relevant range of powder mixture compositions, the formation of nitrogen gas bubbles in an alloy built from the powder mixture composition using full-melt additive manufacturing.

An alloy means a metal composed of at least two metallic elements or at least one metallic element

25 and a non-metallic element, usually formed by solidifying a molten mixture of the metal and at least one other metal or non-metal, homogeneous or having regions with different composition and structure.

An alloy powder includes a powder formed from a single alloy having a defined chemical composition or defined range of chemical compositions, or more than one powder formed from one

30 or more than one alloy, compound, non-metal or elemental metal, which taken together have the defined chemical composition or range of chemical compositions corresponding to the alloy.

An advantage of an alloy powder with disclosed range of compositions is that the alloy powder can be used to form a range of different powder mixture compositions that correspond to the compositions of a range of different steel alloys.

An advantage of a powder mixture composition formed from an additive powder and alloy powder is that the powder mixture composition can be prepared relatively simply, from as few as two different powders.

Where the additive powder is constituted of more than one powder and/or the alloy powder of more than one powder, the order of mixing of the more than one powder constituting the additive powder and the more one powder constituting the alloy powder generally may not affect relevant properties of the resulting powder mixture composition. For example, in the examples described below, it may not have been necessary to completely constitute the $Cr_2N/Cr$ or $Cr_2N/Cr/Cr_3C_2$ additive powder before the constituents of such additive powder were mixed with the 316L or DSS or 420s alloy powder to form the powder mixture composition used in L-PBF AM.

An advantage of a powder mixture composition formed from an additive powder and alloy powder is that a range of powder mixture compositions can be formed using the same additive powder and different alloy powders, and vice versa.

An advantage of preparing a powder mixture composition from an additive powder and alloy powder is that it can be used in the full-melt powder-based additive manufacturing processes to build a range of alloys having different compositions.

An advantage of an alloy powder substantially comprising Ni, Fe, Cr and optionally Mo or Mn is the ability to form a range of powder mixture compositions that can be used in full-melt AM to build components of a range of alloys with increased dissolved nitrogen and chromium contents, and therefore improved mechanical properties and corrosion resistance.

An advantage of a powder mixture composition, by weight percent of the powder mixture composition, substantially comprising no more than 5 wt% N is the ability to form a range of powder mixture compositions that can be used in full-melt AM to build components of a range of alloys with increased dissolved nitrogen content, up the maximum level that can be dissolved, around 2 wt%, depending on the composition of the built alloy, and if above around 2 wt %, containing nitrogen in the form of nitrides.

An advantage of a powder mixture composition, by weight percent of the powder mixture composition, that substantially comprises Cr from 10.5 to 35, Ni up to 38, Mo up to 10 and Mn up to

19, and balance Fe, is the ability to use full-melt AM to build components from a range of high-nitrogen stainless steels having improved mechanical properties and corrosions resistance.

An advantage of a powder mixture composition, by weight percent of the powder mixture composition, that substantially comprises Cr from 0.5 to 50, Fe up to 40, Mo 0 to 30, Mn 0 to 3 and

5    balance Ni, is the ability to use full-melt AM to build components from a range of high nitrogen austenitic nitrogen alloys having improved mechanical properties and corrosions resistance.

In another aspect, the additive powder is between 0.5 and 10 wt% of the powder mixture composition.

An advantage of the additive powder between 0.5 and 10 wt% of the powder mixture composition,

10    is that the composition of available alloy powders can be closely matched to the composition of a component built by full-melt AM using the powder mixture composition.

In another aspect, the additive powder further comprises one or more of an Fe-, Cr-, Mo- or Mn-carbide, and, optionally, one or more of C, Mo or Mn powder.

A Cr-carbide means tri-chromium di-carbide or any stoichiometric or non-stoichiometric compound

15    of chromium and carbon. An Fe-, Mo- or Mn-carbide means any stoichiometric or non-stoichiometric compound of iron, molybdenum or manganese and carbon.  An Fe, Cr-, Mo- or Mn-carbide may be a carbide containing more than one of Fe, Cr, Mo or Mn.

An advantage of adding a carbide of one or more of Fe, Cr, Mo or Mn or C to the additive powder is to allow control over the level of carbon content in the powder mixture composition.

20    An advantage of a powder mixture composition with a controlled carbon content, is the use of C to reduce the O level in alloys built from the powder mixture composition using full-melt additive manufacturing.

Further advantages of a powder mixture composition with a controlled C content include the use of C to assist in suppressing formation of $N_2$ gas bubbles during cooling and the combination of N and C

25    in solid solution to hinder detrimental nitride and carbide formation during cooling in the solid state.

In another aspect, the additive powder further comprises one or more of an Mo- or Mn-nitride powder, and, optionally, one or more of Mo or Mn powder.

A Mo nitride means $Mo_2N$, $MoN$, $MoN_2$ or any stoichiometric or non-stoichiometric compound of molybdenum and nitrogen.  A nitride of Mn means $Mn_3N_2$, $MnN$ or any stoichiometric or non-

30    stoichiometric compound of manganese and nitrogen. A nitride of one or more of Cr, Mo or Mn may be a nitride containing more than one of Cr, Mo or Mn.

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In another aspect, the powder is an austenitic stainless steel comprising, in weight percent: Cr 15 to 26; Ni 0 to 38; Mo 0 to 8; Mn 1 to 19; Si <4.5; N <0.2; C < 0.25, and optionally one or more of P<0.045, S<0.04, Cu<5, Co<0.2, Al<0.6, Ti<0.7, W<2.5, Ta<0.1, V<0.5, Nb<1.1, and balance Fe and unavoidable impurities.

5    In another aspect, the alloy powder is a ferritic stainless steel comprising, in weight percent: Cr 10.5 to 30; Ni 0 to 2.5; Mo 0 to 4.2; Mn 0.3 to 1.5; Si <1; N <0.25; C < 0.2, and optionally one or more of P<0.04, S<0.03, Cu<0.2, Al<0.3, Ti<0.6, Nb<0.8 and balance Fe and unavoidable impurities.

In another aspect, the alloy powder is a duplex stainless steel comprising, in weight percent: Cr 20 to 35; Ni 1 to 10; Mo 0 to 5; Mn 0 to 6; Si <1; N <0.65; C < 0.2, and optionally one or more of P<0.045,

10   S<0.03, Cu<2.5, Ti<0.25, W<1.5, and balance Fe and unavoidable impurities.

In another aspect, the martensitic alloy powder is a martensitic stainless steel comprising, in weight percent: Cr 11 to 18; Ni 0 to 7; Mo 0 to 2; Mn 0 to 1; Si <1; N <0.12; C < 1.2, and optionally one or more of P<0.04, S<0.03, Cu<0.3, Nb<0.3, and balance Fe and unavoidable impurities.

In another aspect, the austenitic stainless alloy powder is an AISI 316 type austenitic stainless steel

15   comprising, in weight percent: Cr 16 to 18; Ni 10 to 14; Mo 2 to 3; Mn<2; Si 1; N <03; C < 0.08, and optionally one or more of P<0.045, S<0.035, Ti<0.7, Nb<1.1, and balance Fe and unavoidable impurities.

In another aspect, the austenitic stainless alloy powder is an AISI 304 type austenitic stainless steel comprising, in weight percent: Cr 18 to 20; Ni 8 to 12; Mn<2; Si 1; N <03; C < 0.08, and optionally one

20   or more of P<0.045, S<0.035, and balance Fe and unavoidable impurities.

In another aspect, the duplex stainless alloy powder is a AISI S31803/2205 duplex stainless steel comprising, in weight percent: Cr 21 to 23; Ni 4.5 to 6.5; Mn<2; Mo 2.5 to 3.5; Si<1; N 0.08 to 0.2; C < 0.03, and optionally one or more of P<0.03, S<0.02, and balance Fe and unavoidable impurities.

In another aspect, the duplex stainless alloy powder is a 2507 duplex stainless steel comprising, in

25   weight percent: Cr 24 to 26; Ni 6 to 8; Mn<1.2; Mo 3 to 5; Si<0.8; N 0.24 to 0.32; C < 0.03, and optionally one or more of P<0.03, S<0.02, Cu<0.5, and balance Fe and unavoidable impurities.

In another aspect, the additive powder can consist of essentially only carbide, including chromium carbide, possibly including chromium powder.

An advantage of such carbide-only additive powders is that carbon does not evaporate from the

30   melt or solidified material, only in combination with oxygen. Also, they can be used to stabilize dendritic as opposed to cellular microstructures

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In yet another aspect, a method for additively manufacturing an alloy component comprising: providing a powder mixture having the above disclosed powder mixture composition; applying a directed heat source to selected regions of the powder mixture to form fully molten regions; and cooling the fully molten regions to form solid alloy regions, wherein the solid alloy regions are

5      disposed to additively form the alloy component.

An alloy component means any alloy structure produced by powder-based full-melt additive manufacturing, including a structure that may require further processing, including physical removal of material, heat treatment, or surface treatment, in order to be suitable for use as a component part of an assembly.

10     A directed heat source means any heat source that is capable of delivering heat to selected regions of powder.

Selected regions of a powder mixture mean parts of the powder mixture that are selected for application of the directed heat source.

A fully melted region means that a selected powder region acted on by the directed heat source

15     becomes molten when so heated and then solidifies, as opposed to a method in which the heated powder particles remain solid and merely fuse together. In fully melted region, formed in full-melt powder-based AM, a fraction of particles in the input powder mixture, particular those having a higher melting point, such as nitrides and carbides, may remain at least partially solid when heated and so be at least partially retained in the built sample.

20     Solid alloy regions mean regions formed by solidification of the fully melted region of the powder mixture composition, having the composition of the powder mixture as opposed to the alloy powder.

An advantage of performing additive manufacturing on such a powder mixture composition is that a range of alloy component compositions may be accessed, in which the alloy component

25     incorporates the components of the additive powder, particularly nitrogen and chromium, allowing components to be built that contain high levels of chromium and nitrogen.

In particular, an advantage of the disclosed powder mixture compositions, consisting essentially of an additive powder and an alloy powder, is that full-melt AM processing of such powder mixture compositions can be used to build a component having a controllable nitrogen content in solid

30     solution, higher than that which could be obtained using the alloy powder alone.

A further advantage of the disclosed powder mixture compositions, consisting essentially of an additive powder and an alloy powder, is that full-melt AM of such powder mixture compositions can

be used to build a component having a dissolved nitrogen content that is distributed essentially uniformly throughout the built component, compared to the dissolved nitrogen distribution in components formed by other processing routes, such as under high nitrogen partial pressure or by surface nitriding.

5    In yet another aspect, the selected regions of powder mixture are located in successive layers of the powder mixture supported in a powder bed.

An advantage of a using powder bed is that components can be fabricated from the powder mixture composition using established powder bed technologies.

In yet another aspect, selected regions of power mixture delivered to a substrate using a nozzle.

10   An advantage of using a powder nozzle is that components can be fabricated from the powder mixture composition using established directed energy deposition technologies.

In yet another aspect, the directed heat source is a laser or an electron beam.

An advantage of the directed heat source being a laser or an electron beam compatibility with established heat delivery technologies. A laser source includes heat direction using mirror and/or

15   fiber-based optical systems.

In yet another aspect, the full-melt L-PBF built component can be subjected to Hot Isostatic Pressing ("HIPping").

An advantage of post-build HIPping is the removal of pores, with the ensuing improvement in corrosion resistance and mechanical properties, which can be accompanied by the dissolving of

20   nitrogen gas from the pores into the component, further improving corrosion resistance and mechanical properties.

In a further aspect, a stainless steel component can consist substantially of austenite with a cellular microstructure, and, by weight percent, Cr at least 15, Mn up to 8 wt%, Mo up to 6 wt%, N at least 0.18 wt% and one or both of a hardness of at least 250 $HV_{0.1}$ and a corrosion MARC number of 16-

25   100

In a further aspect, the stainless steel component can have N at least 0.15 %, and one or both of a hardness of at least 280 $HV_{0.1}$ and a corrosion MARC number of 22-100.

Consisting substantially of austenite means consisting of at least 90 or 95 volume % the austenitic face centered cubic phase.

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In yet another aspect, a stainless steel component can consist substantially of austenite with a dendritic microstructure, and, by weight percent, Cr at least 15, Mn up to 8 wt%, Mo up to 6 wt%, N at least 0.18 wt% and C of at least 0.3 % and a hardness of at least 300 HV0.1.

A cellular microstructure means a metastable structure characteristic of AM occurring within individual grains, the cellular structure being generally cylindrical in shape, possibly with high dislocation density at the cell walls, and elemental segregation between cell interior and walls. Exact cell size, elemental segregation and dislocation structure may vary with process parameters and material chemistry. Example of such cellular microstructure are seen in the high magnification images shown in FIG. 8.

MARC means Measure of Alloying for Resistance to Corrosion and is equal to wt% Cr + 3.3 Mo + 20 N + 20 C – 0.5 Mn – 0.25 Ni.  M.O. Siedel, Mat.-wiss. u. Werkstofftech. vol. 37, No. 10 ()2006) p 875,

Consisting substantially of austenite means consisting of at least 90 or at least 95 volume percent of the austenitic face center cubic phase.

An advantage of an alloy component having such composition and microstructure is improvement in mechanical properties, including increased hardness, strength and ductility, and superior corrosion resistance with respect to an alloy built using full-melt AM from the same or equivalent alloy powder but without the additive powder.

In a further aspect, Cr is at least 18.

An advantage of having a Cr level of at least 18 is further increased corrosion resistance and hardness.

In a further aspect, C is at least 0.1.

Advantages of having a C level of at least 0.1 in solid solution are increased hardness and corrosion resistance, removal of unwanted traces of oxygen from the alloy, and further suppression of development of $N_2$ gas bubbles and $Cr_2N/CrN$/carbides during cooling in the solid state.

BRIEF DESCRIPTION OF THE FIGURES

To the extent that the figures show different ways of implementing the present invention they are not to be construed as limiting to other possible embodiments falling within the scope of the attached claim set.

FIG. 1 is a set of Light Optical Microscopy (LOM) images taken from L-PBF built samples of 316L, 316L + 1 wt% CrN, 316L + 2.5 wt% CrN, 316L + 2.5 wt% $Cr_2N/Cr$, 316L + 2.5 wt% $Cr_2N/Cr$ + 1 wt% $Cr_3C_2$.

FIG. 2 is a pair of Scanning Electron Microscopy ("SEM") images showing overall powder morphology and Cr-distribution within a 316L + 2.5 wt% $Cr_2N/Cr$ powder mixture.

FIG. 3 shows 111 and 002 austenite X-ray diffraction peaks obtained from L-PBF printed 316L and 316L + 2.5 wt% $Cr_2N/Cr$ specimens.

FIG. 4 shows mass loss measurements performed on L-PBF printed 316L and 316L + 2.5 wt% $Cr_2N/Cr$ specimens.

FIG. 5 shows N and O content, measured by Instrumental Gas Analysis (IGA), of 316L, 316L + 2.5 wt% $Cr_2N/Cr$ and 316L + 2.5 wt% $Cr_2N/Cr$ + 1 wt% $Cr_3C_2$ powder/powder mixtures and fiber-based L-PBF printed specimens.

FIG. 6 shows the C content, measured by IGA, of 316L powder and 316L + 2.5 wt% $Cr_2N$ + 1 wt% $Cr_3C_2$ powder mixture, and 316L, 316L + 2.5 wt% $Cr_2N$, and 316L + 2.5 wt% $Cr_2N$ + 1 wt% $Cr_3C_2$ specimens.

FIG. 7 shows 111, 002 and 220 austenite X-ray diffraction peaks obtained from fiber-based L-PBF printed 316L, 316L + 2.5 wt% $Cr_2N/Cr$ and 316L + 2.5 wt% $Cr_2N/Cr$ + 1 wt% $Cr_3C_2$ specimens.

FIG. 8 shows pairs of SEM obtained from fiber-based L-PBF printed 316L, 316L + 2.5 wt% $Cr_2N/Cr$ and 316L + 2.5 wt% $Cr_2N$ + 1 wt% $Cr_3C_2$ specimens

FIG. 9 shows the Nitrogen content, measured by IGA, of the DSS and DSS + 2.5 wt% $Cr_2N/Cr$ powder/powder mixture and fiber-based L-PBF printed specimens.

FIG. 10 shows Light Optical Microscopy (LOM) images of polished cross sections of DSS and DSS + 2.5 wt% $Cr_2N$ fiber-based L-PBF-printed specimens.

FIG. 11 shows tensile strength and elongation from tensile test for 316L and 316L + 2.2 wt% $Cr_xN$ L-PBF-printed specimens.

FIG. 12 shows LOM images of etched cross sections of 316L, 316L + 2.5 wt% $Cr_3C_2$, 316L + 5 wt% $Cr_3C_2$, and 316L + 7.5 wt% $Cr_3C_2$ L-PBF-printed specimens.

FIG. 13 shows SEM images obtained from cross sections of 316L and 316L + 2.5 wt% $Cr_3C_2$ L-PBF-printed specimens.

FIG. 14 shows SEM images obtained from cross sections of 316L + 5 wt% $Cr_3C_2$ and 316L + 7.5 wt% $Cr_3C_2$ L-PBF-printed specimens.

FIG. 15 shows hardness measurements for 316L L-PBF-printed specimens with different additions of $Cr_2N$ and $Cr_3C_2$.

FIG. 16 shows LOM images of etched cross-sections of 420s, 420s + 1 wt% $Cr_xN$ and 420s + 2 wt% $Cr_xN$ L-PBF-printed specimens.

FIG. 17 shows LOM images of etched cross sections of 420s, 420s + 1 wt% $Cr_xN$ + 3 wt %$Cr_3C_2$ and 420s + 2 wt% $Cr_xN$ + 2 wt %$Cr_3C_2$ + 2.75 wt% Cr L-PBF-printed specimens.

5    DETAILED DESCRIPTION

The examples detailed in this section are for stainless steel parts built using full-melt L-PBF and different stainless steel powders mixed with a range of different additive powders. It is anticipated that similar powder mixtures could be used with other full-melt AM techniques, such as, E-PBF, L-DED and E-DED.

10   In L-PBF, a laser, typically $CO_2$, Nd-YAG, or fiber-based, is scanned across the surface of a powder layer formed with a uniform thickness in a powder bed. In the examples detailed in this section, the powder layer is composed of a steel powder of a steel powder mixed with an additive powder. The laser is scanned between powder layer locations distributed across a grid, separated by a hatch spacing, a parameter which, together with powder layer thickness, laser power and scanning speed,

15   may be optimized for use with a given input powder composition.

FIG. 1 shows a set of Light Optical Microscopy ("LOM") images taken from full-melt L-PBF samples built using AISI 316L austenitic stainless steel powder, alone and mixed with different additive powders containing principally Cr and N. In each of the LOM images, samples were etched to highlight microstructure. The black rings mark the presence of undissolved nitride particles. FIG. 1(a)

20   shows a full-melt L-PBF sample built from 316L powder only, FIG. 1(b) a sample built from 316L powder mixed with 1 wt% CrN, FIG. 1(c) a sample built from 316L powder mixed with 2.5 wt% $Cr_2N/Cr$ powder, FIG. 1(d) a sample built from 316L powder mixed with 2.5 wt% CrN powder and FIG. 1(e) a sample built from 316L powder mixed with 2.5 wt% $Cr_2N/Cr$ and 1 wt% $Cr_3C_2$ powder. "$Cr_2N/Cr$" here refers to a specific mixture of $Cr_2N$ powder with 32 wt% metallic Cr powder, as used

25   in EXAMPLES 1 to 3 below, though it is anticipated that other proportions of Cr powder may be used to achieve similar or even better results, as discussed below.

The LOM images in FIG. 1 show markedly different porosity in full-melt L-PBF samples built from 316L powder mixed with $Cr_2N/Cr$ and CrN. The samples built with 316L with 2.5 wt% $Cr_2N/Cr$, FIG. 1(c), and 316L with 2.5 wt% $Cr_2N/Cr$ and 1 wt% $Cr_3C_2$, FIG. 1(e), show a level of porosity similar that

30   of the sample built with 316L only, FIG. 1(a). This observation was confirmed by measurements using the Archimedes method, which showed that the 316L sample without additive powder, FIG. 1(a), had a porosity of $1.10 \pm 0.25$, the 316L with 2.5 wt% $Cr_2N/Cr$ sample, FIG. 1(c), a porosity of $0.89 \pm 0.15$ and the 316L with 2.5 wt% $Cr_2N/Cr$ and 1 wt% $Cr_3C_2$ sample, FIG. 1(e), a porosity $0.90 \pm 0.07$.

Any residual porosity seen in full-melt L-PBF built samples, such as those shown in FIG. 1, may be reduced or removed by a further processing step, such as Hot Isostatic Pressing ("HIPping"), which will tend to drive nitrogen located in pores into solution and so contribute to improved strength and increased corrosion, in addition to the benefits to such properties arising from reduction of removal

5  of pores.

A similar result was observed with full-melt L-PBF samples built from DSS steel, which showed approximately the same level of porosity with and without addition of 2.5 wt% $Cr_2N$/Cr, as detailed in EXAMPLE 3 in relation to FIG. 10 below.

In contrast, full-melt L-PBF samples built from 316L with 1 wt% CrN, FIG. 1(b), and 316L with 2.5 wt%

10  CrN, FIG. 1(d), show levels of porosity significantly greater than the full melt L-PBF sample built with 316L only, FIG. 1(a). This increase in porosity for 316L with 1 or 2.5 wt% CrN, is consistent with the results reported in CN 108941563A, as noted in the background section. In CN 108941563A, addition of 0.5 to 10 wt% of CrN powder to S136 steel powder (Fe Bal.; C 0.38; Si 0.8; Mn 0.5; Cr 13.6; P <0.03; S <0.03) led to porosity levels of over 20 %, sufficient for air permeation of the built

15  component. The porosity level in the 316L with CrN is significantly lower than observed in S136 steel, due to 316L containing higher Cr levels and therefore are able to dissolve more nitrogen.

To a first approximation, the Cr:N ratio of the additive powder and the Cr and N content of the powder mixture composition, which is in turn a function of the additive powder fraction and the Cr and N content of the alloy powder, controls the level of porosity of full-melt L-PBF-built steel

20  samples. Over a range of powder mixture compositions, a Cr:N ratio of 4:1 or lower in the additive powder, as in pure CrN, leads to a high level of porosity, unacceptable for most applications, except, e.g., where air permeability is desired, as in CN 108941563A. A ratio of 12:1, as in $Cr_2N$/32 wt% Cr additive powder, leads to porosity comparable to samples built from steel powder only, as noted above and detailed in EXAMPLES 1, 2 and 3 for 316L and DSS powders. A ratio of 18:1, as in 2.5 wt%

25  $Cr_2N$/Cr and 1 wt% $Cr_3C_2$ additive powder, also leads to porosity comparable to samples built from 316L steel powder only, as detailed in EXAMPLE 2 and shown in FIG. 7.

Additive powders having Cr:N ratios above 4:1, for example, the $Cr_2N$/32 wt% Cr used in EXAMPLES 1 to 3, having a Cr:N ratio of around 12:1, and the 2.5 wt% $Cr_2N$/32 wt% Cr with 1 wt% $Cr_3C_2$ used in EXAMPLE 2, having a Cr:N ratio of around 18:1, can be formed by mixing one or more Cr nitrides, for

30  example, CrN or $Cr_2N$, with Cr, Cr-carbide or Cr-carbo-nitride in different proportions. In some additive powders, the Cr to $Cr_2N$ ratio can be up to an equal amount. Additive powders having Cr:N ratios of around 5:1, 6:1, 7:1, 8:1, 9:1, 10:1, 11:1, 12:1, 13:1, 14:1, 15:1, 16:1, 17:1, 18:1 or above can thus be obtained.

As detailed in the examples below, addition of 2.5 wt% $Cr_2N/Cr$ powder to the steel powder used in full-melt L-PBF, not only builds samples with low porosity, but also increases the level of nitrogen in solid solution in printed samples, above that seen in samples printed from steel powder only. This increased level of dissolved nitrogen is seen in both austenitic 316L steel (EXAMPLES 1 and 2,

5      referencing FIGS. 3, 5 and 7) and as-printed ferritic duplex DSS steel (EXAMPLE 3, referencing FIG.9). Addition of 1 wt% $Cr_3C_2$ powder to the 316L and 2.5 wt% $Cr_2N/Cr$ powder mixture increase the level of dissolved carbon (EXAMPLE 2, referencing FIG. 6).

As also detailed in EXAMPLE 6 below, addition of carbides and nitride powders in L-PBF printing of martensitic stainless steel may be used to increase the austenitic fraction, in the case of nitrogen,

10     slightly, and, in the case of carbon, significantly.

The maximum amount of nitrogen that can be dissolved in a molten steel at 1700 °C can be calculated using empirical equations (1) and (2) in C. Cui et al., Metals vol. 10 (2020) p 61. as around 1.6 wt% N. For molten steel formed from Fe alloy powder with wt% maximum of Cr 35, Mo 8 and Mn 19, this gives an N solubility of 1.63 wt %. Taking account of the possibility of N loss from the

15     powder mixture, and possible increases in accessible N content due to the presence of C in the powder mixture, this gives an upper limit on the wt% N in the powder mixture composition of 1.7, 1.8, 1.9, or up to around 2 wt %.  Other than being dissolved in the built alloy component, some of the nitrogen in the powder mixture composition can also be introduced into the built alloy component in the form of solid nitrides. Taking this additional nitrogen destination in the built

20     component into account, an upper limit on the overall nitrogen content of the powder mixture composition for use in full melt AM would be around 5 wt %. Relatively small amounts of dissolved nitrogen may noticeably affect alloy properties, such that a nitrogen content as low as 0.05 wt% of the powder mixture composition may still affect the properties of an alloy built from such a powder mixture composition by full-melt AM.

25     As further detailed below, full-melt L-PBF samples built from steel powder mixed with 2.5 wt% $Cr_2N/Cr$ powder showed greatly improved hardness over full-melt L-PBF samples built from steel powder alone. Such an increase in hardness, seen in both 316L and DSS samples, can be attributed to the increased levels of nitrogen in solid solution, and to a lesser extent the positive effect on grain-size hardening (Hall Petch). The increased dissolution of carbon in 316L samples built from

30     316L powder mixed with 2.5 wt% $Cr_2N/Cr$ powder and 1 wt% $Cr_3C_2$ powder was accompanied by a further increase in hardness, attributable, as for nitrogen, to the increased concentration of carbon in solid solution (EXAMPLE 2).

As further detailed below, full-melt L-PBF samples built from steel powder with 2.2 wt% $Cr_xN/Cr$ powder showed improved strength (EXAMPLE 4 and FIG. 11).

As also detailed below, full-melt L-PBF samples built from steel powder using only $Cr_3C_2$ additive powder also showed increased hardness, while builds using mixtures of $Cr_3C_2$ and $Cr_xN/Cr$ additive

5      powder exhibited a hardness increase that was apparently offset by increased nitrogen loss with increased carbon content (EXAMPLE 5).

Also shown in FIG. 1 and detailed below, samples built from 316L or DSS powder mixed with 2.5 wt% $Cr_2N/Cr$ powder, and 316L powder mixed with 2.5 wt% $Cr_2N/Cr$ powder and 1 wt% $Cr_3C_2$ powder, showed  microstructures characteristic of L-PBF sample printed from steel only.  In particular, the

10      electron micrographs in FIG. 8, for samples printed form 316L, 316L + 2.5 wt% $Cr_2N/Cr$ and 2.5 wt% $Cr_2N/Cr$ + 1 wt% $Cr_3C_2$ powders, all show characteristic elongated austenite grains that sometimes change direction over a melt-pool. The elongated austenite grains also have a cellular microstructure/substructure, visible in the higher magnification images, which leads to the increased strength-to-ductility ratio, characteristic of 316L processed by full-melt L-PBF, as discussed below in

15      relation to FIG. 8.

As further detailed below, addition of 2.5 wt% $Cr_2N/Cr$ powder also leads to a significant improvement in corrosion resistance observed in samples built from 316L (EXAMPLE 1 and FIG. 4). Such increased corrosion resistance of L-PBF samples upon addition of 2.5 wt% $Cr_2N/Cr$ powder can be attributed to the increase in the amount of nitrogen in solid solution and to a lesser extent to the

20      small relative increase in Cr content. In general, when building stainless steel components, the Cr content in the powder mixture composition may be kept above 10.5 wt%, such that full-melt AM results in a stainless steel component having increased corrosion resistance associated with more than 10.5 wt% Cr content.

Though the additive powders in the examples below correspond to 2.5 wt% and 3.5 wt%, it is

25      anticipated that lower and higher weight fractions of additive powder could be used, 0.5 wt%, 1%, 1.5 % etc, up to 10, 15 or 20 wt%, with the Cr:N ratio (or the Cr/Mn/Mo to N ratio), suitably adjusted to not give rise to nitrogen gas bubbles in alloy samples built from the powder mixture.  The adjustment of the total weight percent of Cr, C and other alloying elements also being suitably adjusted to the given alloy composition to be formed from the given powder mixture. As noted

30      above, the composition of the additive powder can also be adjusted by including C and Cr, Mo, Mn or Fe carbide powders, Mo or Mn elemental powders. The maximum and minimums amount of additive powder, having a range of possible compositions, as noted above, that could be used to create a desired full-melt L-PBF printed alloy composition/property will depend on the particular

alloy system to be printed, but could be as low as around 0.1 wt% and, as already noted, as high as around 20 wt%.In particular, stainless steel alloys, in powder form which could be used in full melt L-PBF, when mixed with additive powders comprising Cr and N, and optionally C and other powders, as outlined above can be used to form powder alloy compositions substantially comprising: N no more than 5, Cr from 10.5 to 35, Ni up to 38, Mo up to 10 and Mn up to 19, and balance Fe.

Such stainless steel alloys in powder form include the following:

- Austenitic stainless steels comprising, in weight percent: Cr 15 to 26; Ni 0 to 38; Mo 0 to 8; Mn 1 to 19; Si <4.5; N <0.9; C < 0.25, optionally one or more of P<0.045, S<0.04, Cu<5, Co<0.2, Al<0.6, Ti<0.7, W<2.5, Ta<0.1, V<0.5, Nb<1.1, and balance Fe and unavoidable impurities, including specific steel types, such as:

    AISI 316 type austenitic stainless steel comprising, in weight percent: Cr 16 to 18; Ni 10 to 14; Mo 2 to 3; Mn<2; Si 1; N <0.3; C < 0.08, optionally one or more of P<0.045, S<0.035, Ti<0.7, Nb<1.1, and balance Fe and unavoidable impurities.

    o AISI 304 type austenitic stainless steel comprising, in weight percent: Cr 18 to 20; Ni 8 to 12; Mn<2; Si 1; N <03; C < 0.08, optionally one or more of P<0.045, S<0.035, and balance Fe and unavoidable impurities.

- Ferritic stainless steel comprising, in weight percent: Cr 10.5 to 30; Ni 0 to 2.5; Mo 0 to 4.2; Mn 0.3 to 1.5; Si <1; N <0.25; C < 0.2, optionally one or more of: P<0.04, S<0.03, Cu<0.2, Al<0.3, Ti<0.6, Nb<0.8, and balance Fe and unavoidable impurities.

- Duplex stainless steels comprising, in weight percent: Cr 20 to 35; Ni 1 to 10; Mo 0 to 5; Mn 0 to 6; Si <1; N <0.65; C < 0.2, optionally one or more of: P<0.045, S<0.03, Cu<2.5, Ti<0.25, W<1.5, and balance Fe and unavoidable impurities, including more specifically steels such as:

    o AISI S31803/2205 duplex stainless steel comprising, in weight percent: Cr 21 to 23; Ni 4.5 to 6.5; Mn<2; Mo 2.5 to 3.5; Si<1; N 0.08 to 0.2; C < 0.03, optionally one or more of P<0.03, S<0.02, and balance Fe and unavoidable impurities.

    o 2507 duplex stainless steel comprising, in weight percent: Cr 24 to 26; Ni 6 to 8; Mn<1.2; Mo 3 to 5; Si<0.8; N 0.24 to 0.32; C < 0.03, optionally one or more of P<0.03, S<0.02, Cu<0.5, and balance Fe and unavoidable impurities.

    o FeCrNiSiCuMoW duplex stainless steel comprising, in weight percent: Cr 24 to 26; Ni 5 to 7; Mn<0.5; Mo 1 to 1.5; Si 1.5 to 2.5; Cu 1.5 to 2.5; W 0.8 to 1.2; N <0.1; C < 0.03, optionally one or more of P<0.03, S<0.02, Cu<0.5, and balance Fe and unavoidable impurities.

- Martensitic stainless steel comprising, in weight percent: Cr 11 to 18; Ni 0 to 7; Mo 0 to 2; Mn 0 to 1; Si <1; N <0.12; C < 1.2, optionally one or more of: P<0.04, S<0.03, Cu<0.3, Nb<0.3, and balance Fe and unavoidable impurities.

Aside from their use as alloy powders, the composition ranges of the above stainless steels can also be used as benchmarks for the composition of the resulting powder mixture compositions, following mixture with the additive powder, including powder mixture compositions with nitrogen contents that exceed the above stainless steel composition ranges. Such high nitrogen powder mixture compositions may be used in full-melt AM to build components having the above stainless steels composition ranges, including components having increased nitrogen contents.

Further, using the full-melt powder-based AM method described in the present application, a stainless steel component can be built having an austenitic, cellular structure, and, by weight percent, Cr at least 15, and N at least 0.18 or 0.15 %, a hardness of at least 280 or 250 $HV_{0.1}$ and/or a corrosion MARC number of 16 or 22-100.) By increasing the Cr and/or C fraction in the powder mixture, a component may be built with Cr at least 18 and/or C at least 0.1. The cellular structure is mainly FCC austenite, though some BCC ferrite can occur, possibly preferentially at the cell walls. Cell size, elemental segregation and dislocation structure may vary with process parameters and material chemistry. Such characteristic cellular structure is believed to provide high strength without sacrificing ductility. See D. Kong et al. Additive Manufacturing, Vol. 38 (Feb. 2021) 101804.

Though the above compositions, and the examples detailed below, are suitable for use with additive powders containing predominantly Cr, it is anticipated that the method may be generalized to include additive powders containing Mn or Mo. These two elements, like Cr, increase nitrogen solubility in liquid iron, albeit to a lesser degree. Specifically, at 1600 °C and atmospheric pressure, Mo and Mn are about a half and quarter as effective as Cr at increasing nitrogen solubility.  See, e.g., J.W. Simmons, cited in the background section, FIG. 2 and related discussion.

It is anticipated that the alloy powder composition could be further modified to access austenitic Ni alloy compositions, since nickel-based alloys with an FCC crystal structure act similarly to austenitic stainless steels in regard to Cr and N alloying, in that addition of nitrogen increases corrosion resistance, hardness, strength and ductility, and the addition of chromium increases the solubility of nitrogen and corrosion resistance, as long as the nitrogen is in solid solution. See, Speidel, H. J. C.; Speidel, M. O. Mater. Manuf. Process. 2004, 19, 95–109. The additive powder composition may also be adjusted for such Ni alloys.

In particular, nickel alloys, in powder form which could be used in full melt L-PBF, when mixed with additive powders comprising Cr and N, and optionally C and other powders, as outlined above can

be used to form powder alloy compositions substantially comprising: Cr from 0.5 to 50, Fe up to 40, Mo 0 to 30, Mn 0 to 3 and balance Ni.

For example, a nickel alloy with, by weight percent of the alloy, Cr 0.5 to 40; Ni 24 to 70; Mo 0 to 30; Mn 0 to 3; Si <3; N <0.6; C < 0.25, optionally one or more of P<0.045, S<0.04, Cu<5, Co<33, Al<3,

5    Ti<2.5, W<5.25, Ta<5.5, V<0.35, Nb<5.5, La<0.1, Zr<0.1, and balance Fe and unavoidable impurities.

Such a nickel alloy could be UNS N06625 type nickel alloy, in weight percent of the alloy:  Cr 20 to 23; Fe < 5; Mn < 2; Si < 0.5; C < 0.01; Co < 1; Mo 8 to 10; Nb 3.15 to 4.15, with optionally one or more of Ti < 0.4, Al < 0.4, P<0.015, S<0.015, and balance Ni and unavoidable impurities.

Such a nickel alloy could also be an UNS N07718 type nickel alloy having, in weight percent of the

10   alloy:  Cr 17 to 21; Ni 50 to 55; Mn < 0.35; Si < 0.35; C < 0.08; Co < 1; Mo 2.8 to 3.3; Nb + Ta 4.75 to 5.5; Ti 0.65 to 1.15; Al 0.2 to 0.8, with optionally one or more of Cu < 0.3, P<0.015, S<0.015, and balance Fe and unavoidable impurities.

By analogy to the stainless steel composition ranges, aside from their use in alloy powders, the composition ranges of the austenitic nickel alloys can also be used as benchmarks for the

15   composition of the resulting powder mixture compositions, following mixture with the additive powder, including powder mixture compositions with nitrogen contents that exceed the above austenitic nickel alloy composition ranges. Such high nitrogen powder mixture compositions may be used in full-melt AM to build components having the above nickel alloy composition ranges composition ranges, including components having increased nitrogen contents.

20   EXAMPLE 1: L-PBF OF AUSTENITIC STAINLESS STEEL (316L) AND $Cr_2N$/Cr

Commercial 20-53 μm-diameter spherical gas-atomized austenitic stainless steel AISI 316L powder was mixed with 2.5 wt% $Cr_2N$/Cr (FSSS 6.9 my) powder, the $Cr_2N$/Cr powder containing 32 wt% pure Cr.  Mixing was done by shaking the powders in a container with glass beads.

This powder mixture was then placed in the powder canister of an Aurora Labs S-titanium Pro $CO_2$-

25   laser powder bed fusion ("L-PBF") system and processed to build 10 x 10 x 7 mm cuboids. The cuboid parts were built in a nitrogen atmosphere, with a pre-heating of 90 °C of the built plate, using 20 mm/s scanning speed, 120 μm hatch spacing, 30 μm layer thickness, 190 W laser power.

Another batch of cuboids was manufactured in the same L-PBF system under similar processing conditions (nitrogen atmosphere, 90 °C pre-heating of the built plate, 40 mm/s scanning speed, 120

30   μm hatch spacing, 30 μm layer thickness and 255 W power) starting from unmixed AISI 316L 45 μm powder.

The chemical composition of the 316L powder and the 316L + 2.5 wt% $Cr_2N$/Cr powder mixture, taken from supplier datasheets and calculated from the relative proportions of $Cr_2N$/Cr powders, with nitrogen content measured by Instrumental Gas Analysis ("IGA"), is as follows:

| Element (wt%) | Fe | Cr | Ni | Mo | Mn | Si | N |
|---|---|---|---|---|---|---|---|
| 316L | Bal. | 17.7 | 12.6 | 2.3 | 0.8 | 0.7 | 0.1 |
| 316L + 2.5 wt% $Cr_2N$ | Bal. | 18.2 | 12.2 | 2.5 | 1.3 | 0.5 | 0.31 |

5      The morphology and uniform mixing of the 316L + 2.5 wt% $Cr_2N$/Cr powder mixture are apparent from Scanning Electron Microscopy ("SEM") images reproduced in FIG. 2. Taken from the same area of powder mixture, FIG. 2(a), a standard SEM image, shows the surface morphology of the powder mixture, and FIG. 2(b) shows an energy dispersive spectroscopy ("EDS") map of Cr Kα-radiation, highlights the distribution of the Cr-containing $Cr_2N$/Cr particles. As seen in FIG. 2, the 316L particles

10     have retained a substantially spherical shape, after mixing with the $Cr_2N$/Cr powder.

The nitrogen content of the L-PBF printed 316L and 316L + 2.5wt% $Cr_2N$/Cr specimens, 0.1 % and 0.31 wt%, respectively, as measured by IGA, was essentially the same as that of the starting 316L powder and powder mixture.

The L-PBF printed 316L and 316L + 2.5wt% $Cr_2N$/Cr specimens exhibit a fully austenitic

15     microstructure, except for sparse and random undissolved nitride particles, as confirmed by X-ray diffraction analysis. FIG. 3 shows (111) and (002) austenite X-ray diffraction peaks obtained, using Cr Kα radiation with a parallel beam geometry, from the 316L and 316L + 2.5wt% $Cr_2N$/Cr specimens. In the 316L + 2.5 wt% $Cr_2N$/Cr specimen, the shift of the (111) and (002) peaks towards lower 2θ angles indicates expansion of the austenite face centered cubic (FCC) lattice with increased nitrogen

20     content in interstitial solid solution.

Addition of 2.5 wt% $Cr_2N$/Cr also significantly increased the hardness of L-PBF printed 316L specimens: from 267 ± 10 $HV_{0.1}$ for 316L to 305 ± 15 $HV_{0.1}$ for 316L + 2.5wt% $Cr_2N$/Cr. Hardness measurements were conducted on single specimens using a Struers DuroScan 70-G5 microhardness tester, a 100 g load, 10 s dwell time, taking the average of at least 39 measurements. Bearing in

25     mind the increase in nitrogen content, from 0.1 wt% for 316L specimen to 0.31 wt% for 316L + 2.5 wt% $Cr_2N$/Cr specimen, as observed by IGA, and the location of nitrogen at interstitial sites in the 316L + 2.5 wt% $Cr_2N$/Cr specimen, as observed by X-ray diffraction, the hardness increase can be

attributed to nitrogen solid solution strengthening, and to an extent the positive effect on grain-size hardening (Hall Petch).

The addition of 2.5 wt% $Cr_2N/Cr$ also significantly increases the corrosion resistance of L-PBF printed 316L specimens. This is indicated by the mass loss measurements, conducted according to modified

5       ASTM G48, by immersion of 9 x 5 x 1 mm coupons in individual test tubes containing 5.6 wt% $FeCl_3$ solution for 10 days at 22 ± 2 °C, as shown in FIG. 4. While the two 316L specimens, two upper lines, corroded significantly during immersion in the aggressive $FeCl_3$ solution, no corrosion was observed on the 316L + 2.5 wt% $Cr_2N/Cr$ specimen. The increased corrosion resistance was evidently not affected by the presence of few undissolved nitride particles.

10      EXAMPLE 2: L-PBF OF AUSTENITIC STAINLESS STEEL (316L) AND $Cr_2N/Cr$ OR $Cr_2N/Cr/Cr_3C_2$

Commercially available gas-atomized AISI 316L powder (having a slightly different composition from that used in EXAMPLE 1) was mixed with 2.5 wt% $Cr_2N/Cr$, containing 32 wt% pure Cr, and further mixed with 1 wt% of $Cr_3C_2$ powder (-325 mesh, or max 45 μm). Powder mixing was done by vacuum mixing, using a "Comfort" mixer supplied by REITEL Feinwerktechnik GmbH.

15      These powder mixtures, 316L + 2.5 wt% $Cr_2N/Cr$ and 316L + 2.5 wt% $Cr_2N/Cr$ + 1 wt% of $Cr_3C_2$, together with a reference batch of unmixed 316L powder, were loaded into a fiber based L-PBF system, and cylindrical specimens, 5 mm diameter and 12 mm high, as well as 12 x 10 x 20 mm cuboids, were built in a nitrogen atmosphere using a 325 mm/s scan speed, 250 W power, 80 μm hatch spacing and 30 μm layer thickness.

20      The chemical composition of the unmixed 316L powder, and the 316L + 2.5 wt% $Cr_2N/Cr$ and 2.5 wt% $Cr_2N/Cr$ + 1 wt% of $Cr_3C_2$ powder mixtures, calculated from the supplier datasheets and proportions of $Cr_2N/Cr/Cr_3C_2$ powders, with nitrogen, oxygen and carbon measured by IGA, are as follows:

| Element (wt%) | 316L | 316L + 2.5wt%$Cr_2N$ | 316L + 2.5 wt%$Cr_2N$ + 1 wt%$Cr_3C_2$ |
|---|---|---|---|
| Fe | 65.7 | 64.0 | 63.4 |
| Cr | 17.0 | 18.9 | 19.6 |
| Ni | 12.5 | 12.2 | 12.1 |
| Mo | 2.5 | 2.4 | 2.4 |
| Mn | 1.4 | 1.4 | 1.4 |
| Si | 0.8 | 0.8 | 0.8 |
| O | 0.0 | 0.1 | 0.1 |
| C | 0.0 | 0.0 | 0.1 |
| N | 0.1 | 0.2 | 0.2 |
|  | 100.0 | 100.0 | 100.0 |

FIG. 5 shows the nitrogen and oxygen content, measured by IGA, of 316L, 316L + 2.5 wt% $Cr_2N/Cr$ and 316L + 2.5 wt% $Cr_2N/Cr$ + 1 wt% $Cr_3C_2$ powder/powder mixtures and fiber-based L-PBF printed specimens. The Nitrogen content of powder mixtures containing 2.5 wt% $Cr_2N/Cr$, with and without 1 wt% $Cr_3C_2$, 0.23 and 0.21 wt%, respectively, is essentially carried over to the fiber-L-PBF printed

5      specimens, 0.21 and 0.19 wt%, respectively. The Oxygen content in the 2.5 wt% $Cr_2N$ L-PBF printed specimen increased significantly, from 0.062 to 0.075 wt%, but decreased in the 2.5 wt% $Cr_2N/Cr$ + 1 wt% $Cr_3C_2$ L-PBF printed specimen, from 0.063 to 0.04 wt%. This indicates an advantage of adding carbon to the 316L/nitride mix, deoxidation, presumably as a result of carbon and oxygen reacting to form CO and/or $CO_2$ gas that then evaporates from the specimen.

10     FIG. 6 shows the carbon content, also measured by IGA, of the 316L powder and 316L + 2.5 wt% $Cr_2N$ + 1 wt% $Cr_3C_2$ powder mixture, and the 316L, 316L + 2.5 wt% $Cr_2N$, and 316L + 2.5 wt% $Cr_2N$ + 1 wt% $Cr_3C_2$ specimens. The carbon content of the 316L + 2.5 wt% $Cr_2N$ + 1 wt% $Cr_3C_2$ powder mixture decreased slightly, by around 0.02 wt%, after fiber-based L-PBF printing, presumably associated with the deoxidation effect mentioned previously. A slight decrease in the carbon content is also noted

15     after fiber-based L-PBF printing for the 316L specimen, from 0.014 to 0.0072 wt%, presumably indicating a small degree of carbon reacting with oxygen leading to deoxidation, slightly offsetting the overall increase in oxygen content.

Addition of 2.5 wt% $Cr_2N$, with and without addition of 1 wt% $Cr_3C_2$, as in EXAMPLE 1, again increased the hardness of fiber-based L-PBF printed 316L specimens, by more than 40 $HV_{0.1}$ for 2.5

20     wt% $Cr_2N$ and by a further 27 $HV_{0.1}$ for 2.5 wt% $Cr_2N$ + 1 wt% $Cr_3C_2$, as follows:

| Fiber-based L-PBF Specimen | Hardness ($HV_{0.1}$) |
|---|---|
| 316L | $258 \pm 14$ |
| 316L+2.5%$Cr_2N$ | $300 \pm 13$ |
| 316L+2.5%Cr2N+1%$Cr_3C_2$ | $327 \pm 16$ |

Such hardening, as already discussed in connection with EXAMPLE 1, can be attributed to nitrogen solution hardening, and to an extent the positive effect on grain-size hardening (Hall Petch), and carbon solid solution strengthening.

As in EXAMPLE 1, fiber-based L-PBF printed 316L, 316L + 2.5 wt% $Cr_2N/Cr$ and 316L + 2.5 wt% $Cr_2N$ +

25     1 wt% $Cr_3C_2$ specimens again exhibited fully austenitic microstructures, as confirmed by X-ray diffraction analysis, except for few undissolved nitride particles, marked by black rings in FIG. 1 c and e. FIG. 7 shows 111, 200 and 220 austenite X-ray diffraction peaks obtained, using Cr Kα radiation with a parallel beam geometry, from 316L and 316L + 2.5wt% $Cr_2N/Cr$ and 316L + 2.5wt% $Cr_2N/Cr$ + 1 wt% $Cr_3C_2$ cuboids. For the 316L + 2.5 wt% $Cr_2N/Cr$ specimens and 316L + 2.5wt% $Cr_2N/Cr$ + 1 wt%

30     $Cr_3C_2$ specimens, the 111, 200 and 220 peaks shift towards lower 2θ angles, indicating expansion of

the austenite FCC lattice by the presence of nitrogen/carbon in interstitial solid solution. In FIG. 7, the FCC lattice expansion is most clearly demonstrated by the shift of the 220 peak.

As shown in the three pairs of SEM images in FIG. 8, the fiber-based L-PBF printed 316L, 316L + 2.5 wt% $Cr_2N/Cr$ and 316L + 2.5 wt% $Cr_2N/Cr$ + 1 wt% $Cr_3C_2$ specimens each exhibit similar
5    microstructures, with characteristic elongated austenite grains that sometimes change direction over a melt-pool. The elongated austenite grains also have an internal cellular substructure, as discussed above, visible in the higher magnification images, which leads to the increased strength-to-ductility ratio, characteristic of 316L processed by L-PBF. Compared to the regular 316L specimen, no additional pore formation was observed In the 316L + 2.5 wt% $Cr_2N/Cr$ and 316L + 2.5 wt% $Cr_2N$ +
10   1 wt% $Cr_3C_2$ specimens, as indicated by the lack of pores in each of the three pairs of micrographs in FIG. 8.

EXAMPLE 3: L-PBF OF DUPLEX STAINLESS STEEL AND $Cr_2N/Cr$

Commercially available duplex stainless steel (DSS) powder was mixed with 2.5 wt% $Cr_2N/Cr$ (again containing 32% wt% Cr). The DSS + 2.5 wt% $Cr_2N/Cr$ powder mixture, together with a reference
15   batch of unmixed DSS powder, were loaded into the fiber-based L-PBF system used in EXAMPLE 2, and cylindrical specimens, 5 mm diameter and 12 mm high and cuboids, 12 x 10 x 20 mm, were built under the same processing conditions as used in EXAMPLE 2.

The chemical composition of the unmixed DSS powder, and the DSS + 2.5 wt% $Cr_2N/Cr$ powder mixture, calculated from the supplier datasheets and proportions of $Cr_2N/Cr$ powder, with nitrogen,
20   measured by IGA, are as follows:

| Element (wt%) | DSS | DSS + 2.5 wt% $Cr_2N$ |
|---|---|---|
| Fe | Bal. | Bal. |
| Cr | 25 | 27 |
| Ni | 6 | 6 |
| Si | 1.8 | 1.8 |
| Cu | 2 | 2 |
| Mo | 1.2 | 1.2 |
| W | 0.9 | 0.9 |
| Mn | 0.1 | 0.1 |
| O | 0.04 | 0.04 |
| N | 0.01 | 0.13 |
| | 100.0 | 100.0 |

Though bulk DSS typically contains around 0.16 wt% Nitrogen, the DSS powder used here has a much lower nitrogen content. Addition of $Cr_2N/Cr$ powder to the DSS powder provides a total N content close to the bulk DSS specification.

FIG. 9 shows the Nitrogen content, measured by IGA, of the DSS and DSS + 2.5 wt% $Cr_2N$/Cr powder/powder mixture and fiber-based L-PBF printed specimens. The nitrogen content of the DSS + 2.5 wt% $Cr_2N$/Cr specimen, 0.138 wt%, is slightly greater than that of DSS + 2.5 wt% $Cr_2N$/Cr powder mixture, 0.128 wt%, presumably as the result of some nitrogen uptake from the nitrogen

5       atmosphere during fiber-based L-PBF. A more significant nitrogen increase is observed for the DSS specimen, 0.046 wt%, compared to the DSS powder, 0.007 wt%, presumably also due to nitrogen absorption from the atmosphere during fiber-based L-PBF, but still a significantly smaller increase than that realized by addition of 2.5 wt% $Cr_2N$ powder.

FIG. 10 shows Light Optical Microscopy (LOM) images of polished cross sections of DSS and DSS + 2.5

10      wt% $Cr_2N$ fiber-based L-PBF-printed specimens. Addition of 2.5 wt% $Cr_2N$ has resulted in no unusual pore types associated with fiber-based L-PBF processing. Also, most $Cr_2N$ particles are fully melted/dissolved during L-PBF, although a few undissolved particles were found near lack-of-fusion defects. The black ring shows an undissolved $Cr_2N$ particle close to a lack-of-fusion defect.

X-ray diffraction analysis (not shown) indicates that the fiber-based L-PBF specimens are ferritic in

15      the as-printed condition, for both the regular DSS and the DSS + 2.5 wt% $Cr_2N$/Cr. It is therefore necessary to perform heat treatment to achieve the duplex structure, as is common for L-PBF printed duplex specimens.

The as-printed hardness of the duplex stainless steel specimen was significantly improved, by the addition of 2.5 wt% $Cr_2N$/Cr in the powder before L-PBF. The hardness increased to 424 ± 16 HV0.1,

20      from the 352 ± 12 HV0.1 of the regular L-PBF duplex stainless steel.

EXAMPLE 4: L-PBF OF AUSTENITIC STAINLESS STEEL (316L) AND $Cr_xN$/Cr

20-53 μm diameter AISI 316L powder was mixed with 2.2 wt% $Cr_xN$/Cr ($CrN$/$Cr_2N$, Fisher number of 1.2 μm, and 30 wt% Cr powder, D50 of 5-10 μm) having 8.3 wt% N.

The chemical composition of the 316L powder and the 316L + 2.2 wt% $Cr_xN$/Cr powder mixture,

25      taken from supplier datasheets and calculated from the relative proportions of the $Cr_xN$/Cr powders, with nitrogen and oxygen content measured by IGA, are as follows:

| Element (wt%) | Fe | Cr | Ni | Mo | Mn | Si | O | C | N |
|---|---|---|---|---|---|---|---|---|---|
| 316L | 65.1 | 17.2 | 12.7 | 2.5 | 1.5 | 0.8 | 0.0 | 0.0 | 0.1 |
| 316L + 2.2 wt% $Cr_xN$/Cr | 63.7 | 18.8 | 12.4 | 2.4 | 1.4 | 0.8 | 0.0 | 0.0 | 0.3 |

The 316L + 2.2 wt% $Cr_xN$/Cr powder mixture was loaded into an SLM®280 fiber based L-PBF system from SLM Solutions (Lübeck, Germany) and printed using a 50 µm layer thickness, 100 µm hatch spacing, a power of 300 W and a scan speed of 850 mm/s. The build platform was kept at 100 °C, and a nitrogen atmosphere was employed, with oxygen content in the chamber kept below 0.1 %.

5    Vertical cuboids of 60 x 12 x 12 mm were built for nitrogen and oxygen determination by IGA. The nitrogen content of the parts were measured to 0.235 ± 0.002 wt%, which is lower than the nitrogen content measured in the powder, 0.319 ± 0.001 wt%. A significant nitrogen loss therefore occurred during L-PBF of the powder mixture, as previously observed. Consistent with previous experiments, the oxygen content was lowered during L-PBF processing, falling from 0.062 ± 0.002 wt%, in the

10   powder, to 0.056 ± 0.001 wt%, in the built parts.

16 tensile test specimens, 13 vertical and 3 horizontal, were built and tested in the following conditions: 5 vertical, untreated; 5 vertical, machined; 3 vertical, stress-relieved at 550 °C for 3 hours and machined; and 3 horizontal, stress-relieved at 550 °C for 3 hours and machined.

The tensile properties of the 316L + 2.2 wt% $Cr_xN$/Cr parts were measured and compared to the

15   tensile properties of 316L parts built on the exact same system, also in nitrogen. The results are shown in Figure 11, with tensile strength and elongation from tensile test obtained according to ISO 6892-1, which compares the tensile properties of 316L printed by L-PBF and 316L + 2.2 wt% $Cr_xN$/Cr printed by L-PBF.

As shown in FIG. 11, the 316L + 2.2 wt% $Cr_xN$/Cr parts show significantly enhanced strength, by 16% -

20   34%, accompanied by a 7-22% reduction in elongation, while the as-built direct comparison gives a 16 % enhanced tensile strength with an 11% lower elongation. As further shown in FIG. 11, both machining and heat treatment enhance the tensile strength, while strength can be further enhanced by 5% while also regaining 5% elongation by a heat treatment at 550°C, followed by machining. Furthermore, as also shown in FIG. 11, the horizontal specimens showed a higher tensile strength

25   and lower elongation, compared to the vertical specimens.

EXAMPLE 5: L-PBF OF AUSTENITIC STAINLESS STEEL (316L) AND $Cr_3C_2$

AISI 316L 20-53 µm powder was mixed with 2.5, 5 and 7.5 wt% of $Cr_3C_2$ powder (Fisher number of 3 µm and a carbon content of 13.1 wt%). The chemical composition of the 316L powder and the 316L + $Cr_3C_2$ powder mixtures, taken from supplier datasheets and calculated from the relative

30   proportions of the $Cr_xN$/Cr powders, with nitrogen content measured by IGA, are as follows:

| Element (wt%) | 316L | 316L + 2.5 wt%$Cr_3C_2$ | 316L + 5 wt%$Cr_3C_2$ | 316L + 7.5 wt%$Cr_3C_2$ |
|---|---|---|---|---|
| Fe | 65.6 | 64.0 | 62.4 | 60.7 |
| Cr | 17.0 | 18.7 | 20.5 | 22.2 |

| | | | | |
|----|------|------|------|------|
| Ni | 12.5 | 12.2 | 11.9 | 11.6 |
| Mo | 2.5  | 2.4  | 2.4  | 2.3  |
| Mn | 1.4  | 1.4  | 1.3  | 1.3  |
| Si | 0.8  | 0.8  | 0.8  | 0.7  |
| O  | 0.0  | 0.0  | 0.0  | 0.0  |
| C  | 0.0  | 0.3  | 0.7  | 1.0  |
| N  | 0.1  | 0.1  | 0.1  | 0.1  |

The above three powder mixtures—316L with 2.5, 5 and 7.5 wt% of $Cr_3C_2$—and a regular 316L reference batch were L-PBF-printed in a home-built system (for details see Andersen, S. A. (2020). Open Architecture Laser Power Bed Additive Manufacturing, Ph.D. thesis, Technical University of Denmark, available at

5      https://backend.orbit.dtu.dk/ws/portalfiles/portal/259025111/Revised_Phd_Thesis_Sebastian_Aaga ard_Andersen_side_1_197_.pdf) using a 40 µm layer thickness.

After a parameter study, parts printed with the following parameters were chosen for analysis:

- 316L and 316L + 5 wt% $Cr_3C_2$: 150 mm/s scan speed, 160 W power, 80 µm hatch spacing.
- 316L + 2.5 wt% $Cr_3C_2$ and 316L + 7.5 wt% $Cr_3C_2$: 150 mm/s scan speed, 225 W power, 100 µm

10                 hatch spacing.

Fiber L-PBF of the 316L and $Cr_3C_2$ mixtures lead to a significant enhancement in carbon content of the final part, and no significant loss in carbon content from powder to parts, as shown by IGA measurements of carbon content, as follows:

| Powder | $Cr_3C_2$ (wt%) | C content powder (wt%) | C content parts (wt%) |
|--------|-----------------|------------------------|-----------------------|
| 316L | 0 | $0.0138 \pm 0.0003$ | $0.0081 \pm 0.0004$ |
| 316L + 2.5 wt% $Cr_3C_2$ | 2.5 | $0.356 \pm 0.005$ | $0.338 \pm 0.020$ |
| 316L + 5 wt% $Cr_3C_2$ | 5 | $0.678 \pm 0.002$ | $0.711 \pm 0.007$ |
| 316L + 7.5 wt% $Cr_3C_2$ | 7.5 | $1.031 \pm 0.004$ | $1.051 \pm 0.020$ |

15      FIG. 12 shows Light Optical Micrographs of etched cross sections of parts built using the above-noted processing parameters from 316L, 316L + 2.5 wt% $Cr_3C_2$, 316L + 5 wt% $Cr_3C_2$, and 316L + 7.5 wt% $Cr_3C_2$. As is apparent from FIG. 12, addition of 2.5 wt% $Cr_3C_2$ led to the formation of vertical cracks, 5 wt% $Cr_3C_2$ to the formation of fewer vertical cracks, and 7.5 wt% $Cr_3C_2$ to no formation of such vertical cracks. It is believed that the vertical cracks seen in the ~2.5-5 wt% $Cr_3C_2$ range may be

20      avoided by use of different processing parameters, though no further optimization was pursued. As

also apparent from the LOMs, for the parts built from 7.5 wt% $Cr_3C_2$ powder mixture, solidification is dendritic instead of cellular, as seen for the 2.5 and 5 wt% $Cr_3C_2$ parts.

As apparent from the higher magnification SEM images of electropolished cross sections shown in FIGS. 13 and 14, an additional phase is formed at the cell boundaries in the 2.5 wt% $Cr_3C_2$ parts, while the dendritic microstructure already appears alongside the cellular microstructure in the 5 wt% $Cr_3C_2$ parts. It is believed that this transition from cellular to dendritic solidification may also depend on the printing parameters, not exclusively on $Cr_3C_2$ content.

FIG. 15 shows hardness values, measured with Vickers hardness indentation on polished cross sections, for the above-noted 316L only and 316L with 2.5, 5 and 7.5 wt% $Cr_3C_2$ L-PBF-printed parts. FIG. 15 also shows hardness results obtained from 316L + $Cr_xN$/Cr and 316L + $Cr_xN$ + $Cr_3C_2$ L-PBF parts, printed on the same setup, using the same 316L and $Cr_3C_2$ powders. The $Cr_xN$ mixture in the 316L + 2.5 wt% $Cr_xN$ specimens was the same as used in EXAMPLE 4, while for the 316L+ $Cr_3C_2$ + CrxN parts, the $Cr_xN$ did not contain Cr, and therefore had 12.75 wt% N.  This difference results in 316L+ $Cr_3C_2$ + 1.75 $Cr_xN$ and 316L + 2.5 wt% $Cr_xN$ specimens. The hardness values in FIG. 15 show a clear increase in hardness with addition of $Cr_3C_2$.

The addition of $Cr_3C_2$ was more effective at increasing hardness than $Cr_xN$ for additions above 2.5 wt%. This difference is attributed to nitrogen loss by evaporation during melting.

Addition of 1 wt% or 2.5 wt% $Cr_3C_2$ to 1.75 wt% $Cr_xN$ resulted in a similar hardness as 5 wt% $Cr_xN$. It is believed that adding more $Cr_3C_2$ to an AISI 316 + $Cr_xN$ mixture does not necessarily lead to a greater hardness increase, an effect which is thought to be caused by more nitrogen loss on adding more $Cr_3C_2$.

EXAMPLE 6: L-PBF OF MARTENSITIC STAINLESS STEEL (420S) AND $Cr_xN$/Cr

AISI 420s 20-53μm powder was mixed with $Cr_xN$ (Fisher number of 1.2 μm and 12.75 wt% N), Cr (D50 of 5-10 μm) and $Cr_3C_2$ powder (Fisher number of 3 μm and a carbon content of 13.1 wt%) in the following proportions: 1 wt% $Cr_xN$ ; 2 wt% $Cr_xN$; 1 wt% $Cr_xN$ and 3 wt% $Cr_3C_2$; 2 wt% $Cr_xN$, 2 wt% $Cr_3C_2$ 2.7 wt% Cr. The chemical compositions of the 420s powder and these powder mixtures, calculated from supplier datasheets and the relative proportions of $Cr_xN$/Cr/$Cr_3C_2$ powders, with nitrogen content measured by IGA, are as follows:

| Element (wt%) | 420s | 420s + 1 wt% $Cr_xN$ | 420s + 2 wt% $Cr_xN$ | 420s + 1 wt% $Cr_xN$ + 3 wt% $Cr_3C_2$ | 420s + 2 wt% $Cr_xN$ + 2 wt% $Cr_3C_2$ + 2.75 Cr |
|---|---|---|---|---|---|
| Fe | 85.5 | 84.6 | 83.8 | 82.1 | 79.7 |
| Cr | 12.8 | 13.5 | 14.3 | 15.8 | 18.2 |
| Mn | 1.0 | 1.0 | 1.0 | 1.0 | 0.9 |
| Si | 0.4 | 0.4 | 0.4 | 0.4 | 0.4 |
| O | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |

| C | 0.2 | 0.2 | 0.2 | 0.6 | 0.5 |
| N | 0.1 | 0.2 | 0.3 | 0.2 | 0.3 |

The above four mixtures and a regular 420s reference batch were printed in an L-PBF system (the same home-built system as used in EXAMPLE 5) using a 30 μm layer thickness. After a parameter study, parts printed with the following parameters were chosen for analysis:

5  - 420s: 490 mm/s scan speed, 226 W power, 80 μm hatch spacing.

   - 420s + 1 wt% $Cr_xN$: 300 mm/s scan speed, 205 W power, 80 μm hatch spacing.

   - 420s + 2 wt% $Cr_xN$: 277 mm/s scan speed, 226 W power, 80 μm hatch spacing.

   - 420s +1 wt% $Cr_xN$ + 3 wt% $Cr_3C_2$ and 420s +2 wt% $Cr_xN$ + 2 wt% $Cr_3C_2$+ 2.75 wt% Cr: 490 mm/s scan speed, 226 W power, 120 μm hatch spacing.

10

For the 420s, 420s + 1 wt% $Cr_xN$, 420s + 2 wt% $Cr_xN$, 420s + 1 wt% $Cr_xN$ + 3 wt %$Cr_3C_2$ and 420s + 2 wt% $Cr_xN$ + 2 wt %$Cr_3C_2$ + 2.75 Cr powder mixtures and built parts, the carbon and nitrogen content was measured by IGA and, for the built parts, the volume percent of austenite fraction in the microstructure was determined by X-ray diffraction analysis and the hardness by Vickers

15  indentation, as follows:

| Name | Austenite fraction (vol%) | Hardness ($HV_{0.2}$) | N content measured powder (wt%) | N content measured parts (wt%) | C content measured powder (wt%) | C content measured parts (wt%) |
|------|------|------|------|------|------|------|
| 420s | 14 | 532 ± 31 | 0.086 ± 0.002 | 0.077 ± 0.001 | 0.248 ± 0.002 | 0.215 ± 0.001 |
| 420s + 1 wt% $Cr_xN$ | 23 | 518 ± 24 | 0.210 ± 0.026 | 0.139 ± 0.001 | 0.244 ± 0.002 | 0.205 ± 0.003 |
| 420s + 2 wt% $Cr_xN$ | 22 | 544 ± 34 | 0.324 ± 0.004 | 0.185 ± 0.005 | 0.231 ± 0.001 | 0.199 ± 0.001 |
| 420s + 1 wt% $Cr_xN$ + 3 wt %$Cr_3C_2$ | 89 | - | 0.225 ± 0.003 | 0.165 ± 0.001 | 0.664± 0.007 | 0.641 ± 0.003 |
| 420s + 2 wt% $Cr_xN$ + 2 wt %$Cr_3C_2$ + 2.75 Cr | 73 | 401 ± 30 | 0.349 ± 0.003 | 0.266 ± 0.006 | 0.501 ± 0.003 | 0.462 ± 0.007 |

As is apparent from the above measurements, for 420s, a significant fraction of the added nitrogen is still lost during L-PBF, while carbon loss is less significant. The addition of nitrogen increases the austenite fraction slighty, while the addition of carbon significantly increase the austenite fraction.

The increased austenite fraction is, as expected, accompanied by a loss of hardness in most specimens.

FIGS. 16 shows LOMs of etched cross-sections of L-PBF 420s, 420s + 1 wt% $Cr_xN$ and 420s + 2 wt% $Cr_xN$ built parts, while FIG. 17 shows LOMS of etched cross-sections of L-PBF 420s, 420s + 1 wt% $Cr_xN$

5    + 3 wt %$Cr_3C_2$ and 420s + 2 wt% $Cr_xN$ + 2 wt %$Cr_3C_2$ + 2.75 Cr built parts.

The microstructures seen in FIGS. 16 and 17 show that the martensitic microstructure of as-built 420s  does not change much with the addition of 1 or 2 wt% $Cr_xN$, except for shallower melt-pools and more intrinsic ageing. With the further addition of $Cr_3C_2$, and possibly also Cr, the microstructure clearly changes, consistent with the higher austenite fraction observed by XRD. The grains are now

10    much larger, with a cellular-dendritic substructure.

Although the present invention has been described in connection with the specified embodiments, it should not be construed as being in any way limited to the presented examples. The scope of the present invention is set out by the accompanying claim set. In the context of the claims, the terms "comprising" or "comprises" do not exclude other possible elements or steps. Also, the mentioning

15    of references such as "a" or "an", etc., should not be construed as excluding the plurality. The use of reference signs in the claims with respect to elements indicated in the figures shall also not be construed as limiting the scope of the invention. Furthermore, individual features mentioned in different claims, may possibly be advantageously combined, and the mentioning of these features in different claims does not exclude that a combination of features is not possible and advantageous.

SUBSTITUTE SHEET (RULE 26)

CLAIMS

1. A powder mixture composition consisting essentially of:

   - up to 20 weight percent of an additive powder substantially comprising a chromium nitride powder and, optionally, chromium powder, wherein, by weight percent of the additive powder, the Cr:N ratio is greater than 4

   and

   - balance of an alloy powder substantially comprising Fe, Cr, and Ni, and optionally Mo and Mn

   wherein, by weight percent of the powder mixture composition, the powder mixture substantially comprises N no more than 5 and:

   - Cr from 10.5 to 35, Ni up to 38, Mo up to 10 and Mn up to 19, and balance Fe,

   or

   - Cr from 0.5 to 50, Fe up to 40, Mo 0 to 30, Mn 0 to 3 and balance Ni.

2. The powder mixture composition of claim 1, wherein the additive powder comprises between 0.5 and 10 wt%.

3. The powder mixture composition of claim 1 or 2, wherein the additive powder further comprises one or more of an Fe-, Cr-, Mo- or Mn-carbide powder and optionally one or more of Fe, Mo, Mn or C powder.

4. The powder mixture composition of any of claims 1 to 3, wherein the additive powder further comprises one or more of an Mo- or Mn-nitride powder, and, optionally, one or more of Mo or Mn powder.

5. The powder mixture composition of any of claims 1 to 4, wherein the alloy powder is an austenitic stainless steel comprising, in weight percent: Cr 15 to 26; Ni 0 to 38; Mo 0 to 8; Mn 1 to 19; Si <4.5; N <0.9; C < 0.25, and optionally one or more of P<0.045, S<0.04, Cu<5, Co<0.2, Al<0.6, Ti<0.7, W<2.5, Ta<0.1, V<0.5, Nb<1.1, and balance Fe and unavoidable impurities.

6. The powder mixture composition of any of claims 1 to 4, wherein the alloy powder is a ferritic stainless steel comprising, in weight percent: Cr 10.5 to 30; Ni 0 to 2.5; Mo 0 to 4.2; Mn 0.3 to 1.5; Si <1; N <0.25; C < 0.2, and optionally one or more of P<0.04, S<0.03, Cu<0.2, Al<0.3, Ti<0.6, Nb<0.8 and balance Fe and unavoidable impurities.

5

7. The powder mixture composition of any of claims 1 to 4, wherein the alloy powder is a duplex stainless steel comprising, in weight percent: Cr 20 to 35; Ni 1 to 10; Mo 0 to 5; Mn 0 to 6; Si <1; N <0.65; C < 0.2, and optionally one or more of P<0.045, S<0.03, Cu<2.5, Ti<0.25, W<1.5, and balance Fe and unavoidable impurities.

10

8. The powder mixture composition of any of claims 1 to 4, wherein the alloy powder is a martensitic stainless steel comprising, in weight percent: Cr 11 to 18; Ni 0 to 7; Mo 0 to 2; Mn 0 to 1; Si <1; N <0.12; C < 1.2, and optionally one or more of P<0.04, S<0.03, Cu<0.3, Nb<0.3, and balance Fe and unavoidable impurities.

15

9. The powder mixture composition of claim 5, wherein the austenitic stainless steel alloy powder is an AISI 316 type austenitic stainless steel comprising, in weight percent: Cr 16 to 18; Ni 10 to 14; Mo 2 to 3; Mn<2; Si 1; N <03; C < 0.08, and optionally one or more of P<0.045, S<0.035, Ti<0.7, Nb<1.1, and balance Fe and unavoidable impurities.

20

10. The powder mixture composition of claim 5, wherein the austenitic stainless steel alloy powder is an AISI 304 type austenitic stainless steel comprising, in weight percent: Cr 18 to 20; Ni 8 to 12; Mn<2; Si 1; N <03; C < 0.08, and optionally one or more of P<0.045, S<0.035, and balance Fe and unavoidable impurities.

25

11. The powder mixture composition of claim 7, wherein the duplex stainless steel alloy powder is a AISI S31803/2205 duplex stainless steel comprising, in weight percent: Cr 21 to 23; Ni 4.5 to 6.5; Mn<2; Mo 2.5 to 3.5; Si<1; N 0.08 to 0.2; C < 0.03, and optionally one or more of P<0.03, S<0.02, and balance Fe and unavoidable impurities.

30

12. The powder mixture composition of claim 7, wherein the stainless alloy powder is a 2507 duplex stainless steel comprising, in weight percent: Cr 24 to 26; Ni 6 to 8; Mn<1.2; Mo 3 to 5; Si<0.8; N 0.24 to 0.32; C < 0.03, and optionally one or more of P<0.03, S<0.02, Cu<0.5, and balance Fe and unavoidable impurities.

30

13. Any of the powder mixtures of claims 1 to 13, wherein the powder mixture is essentially free of boron.

14. Any of the powder mixtures of claims 1 to 13, wherein the Cr:N ratio is greater than 8.

15. Any of the powder mixtures of claims 3 to 14, wherein the additive powder is essentially chromium carbide and optionally chromium.

16. A method for additively manufacturing an iron or nickel or chromium based alloy component comprising:

providing a powder mixture having the composition of any of claims 1 to 15;

applying a directed heat source to selected regions of the powder mixture to form fully molten regions; and

cooling the fully molten regions to form solid alloy regions, wherein the solid alloy regions are disposed to additively form the alloy component.

17. The method of claim 16, wherein the selected regions of powder mixture are located in successive layers of the powder mixture supported in a powder bed or are delivered to a substrate using a nozzle.

18. The method of any of claims 16 to 17, wherein the directed heat source is a laser or an electron beam.

19. A component made using any of the methods of claims 15 to 18 and any of the powder compositions of claims 1 to 14.

20. A stainless steel component consisting substantially of austenite with a cellular microstructure, and, by weight percent, Cr at least 15, Mn up to 8 wt%, Mo up to 6 wt%, N at least 0.18 wt% and one or both of a hardness of at least 250 HV0.1 and a corrosion MARC number of 16-100.

21. A stainless steel component consisting substantially of austenite with a cellular microstructure, and, by weight percent, Cr at least 15, Mn up to 8 wt%, Mo up to 6 wt%, N at least 0.15 %, and one or both of a hardness of at least 280 HV0.1 and a corrosion MARC number of 22-100.

22. A stainless steel component consisting substantially of austenite with a dendritic microstructure, and, by weight percent, Cr at least 15, Mn up to 8 wt%, Mo up to 6 wt%, N at least 0.15 %, and C of at least 0.3% and a hardness of at least 300 HV0.1.
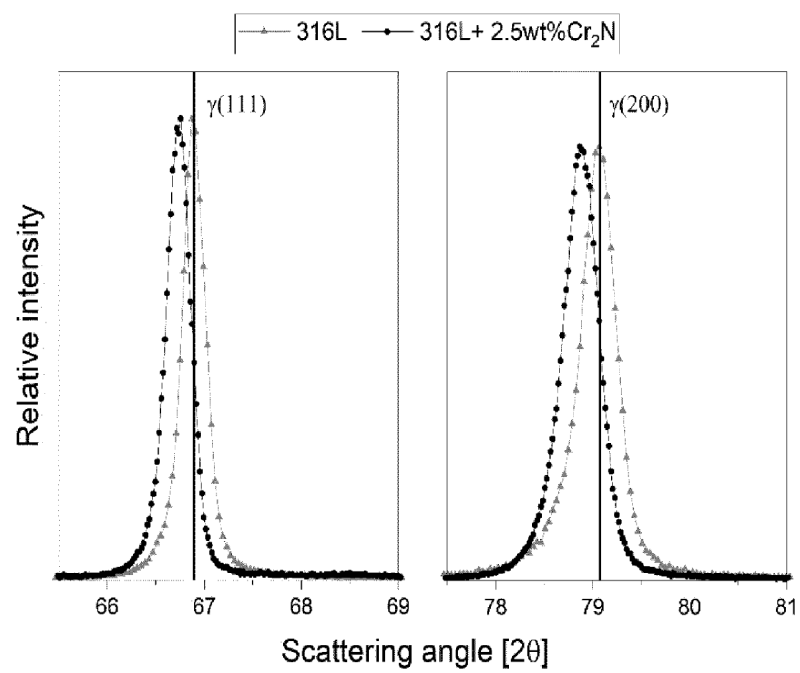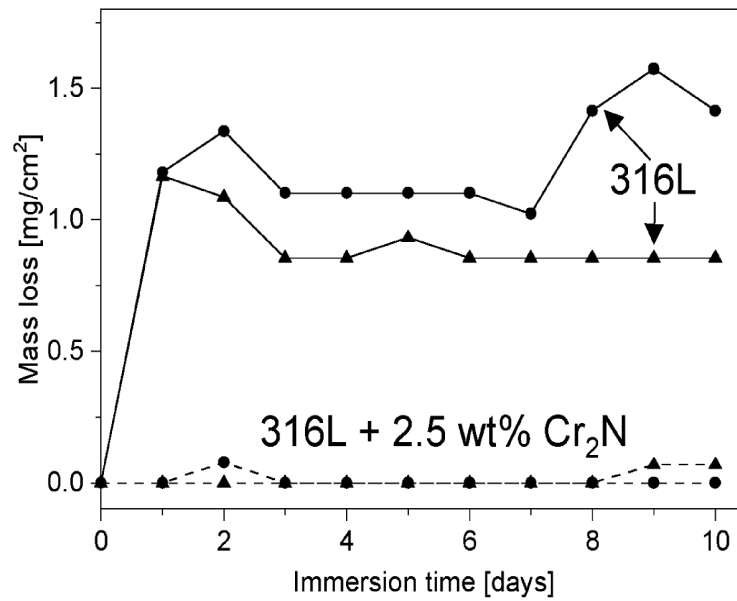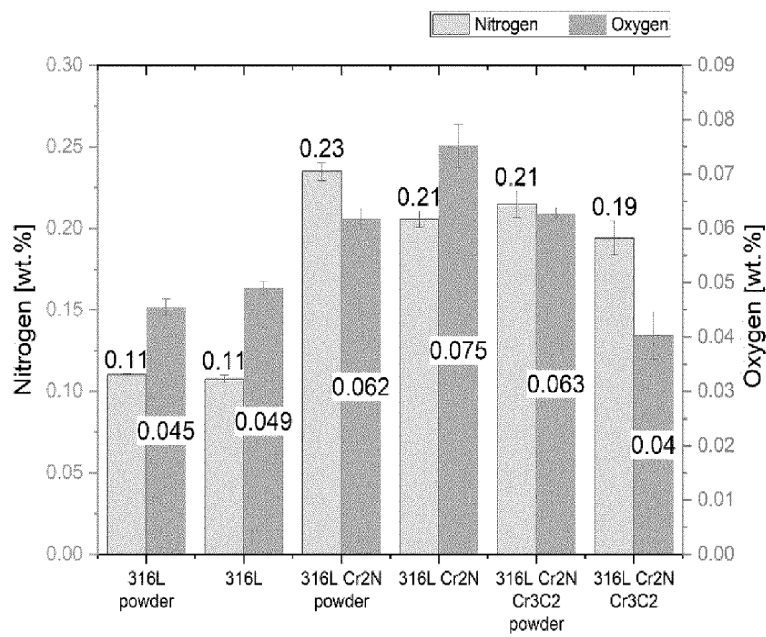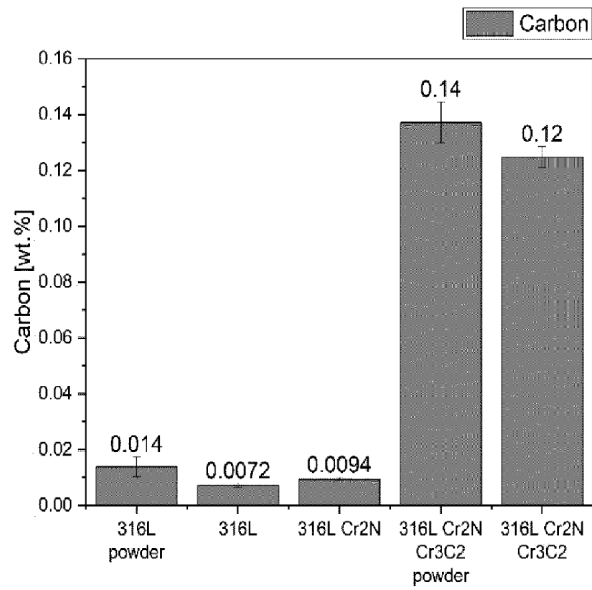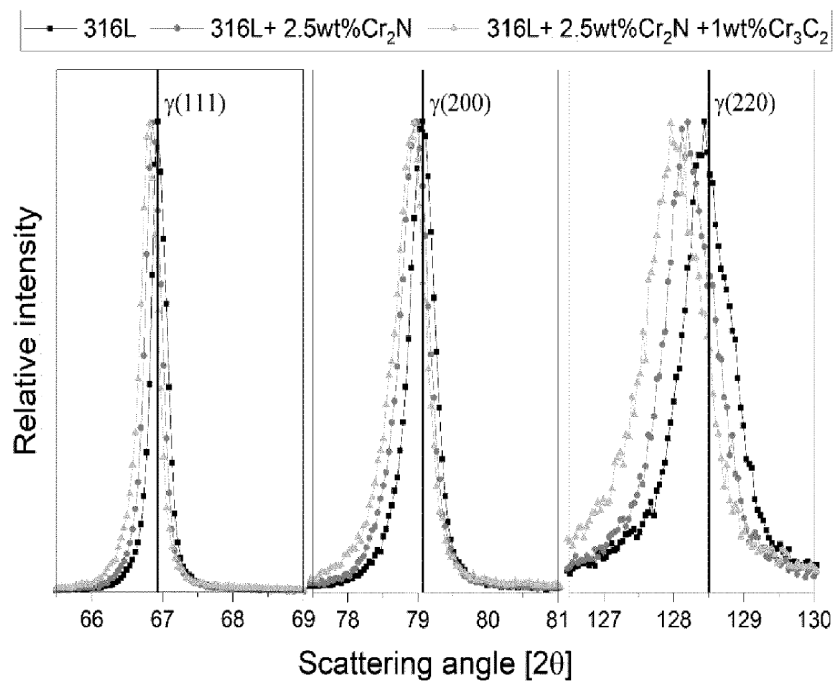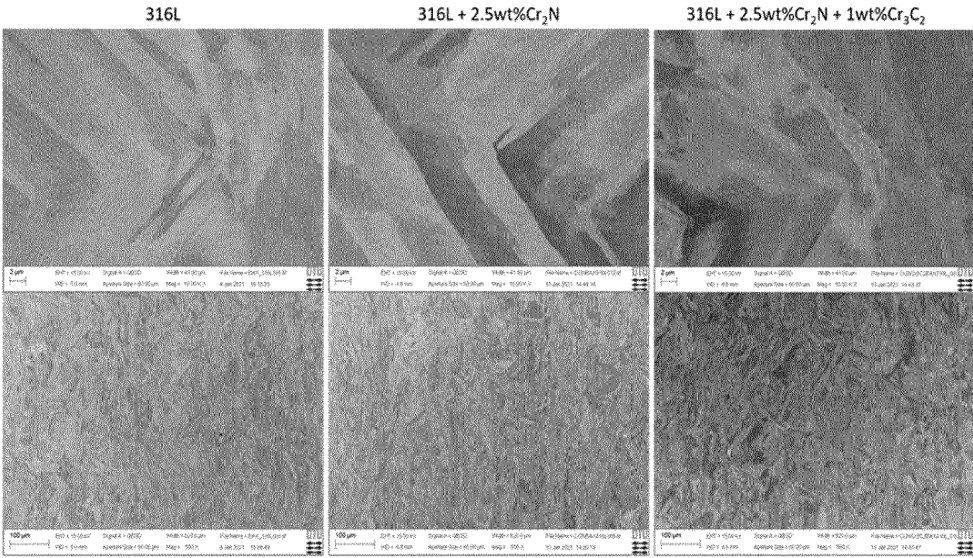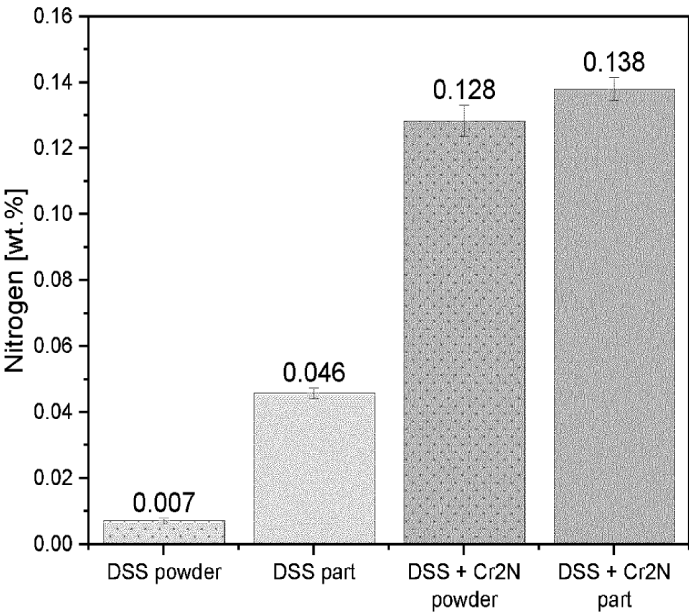
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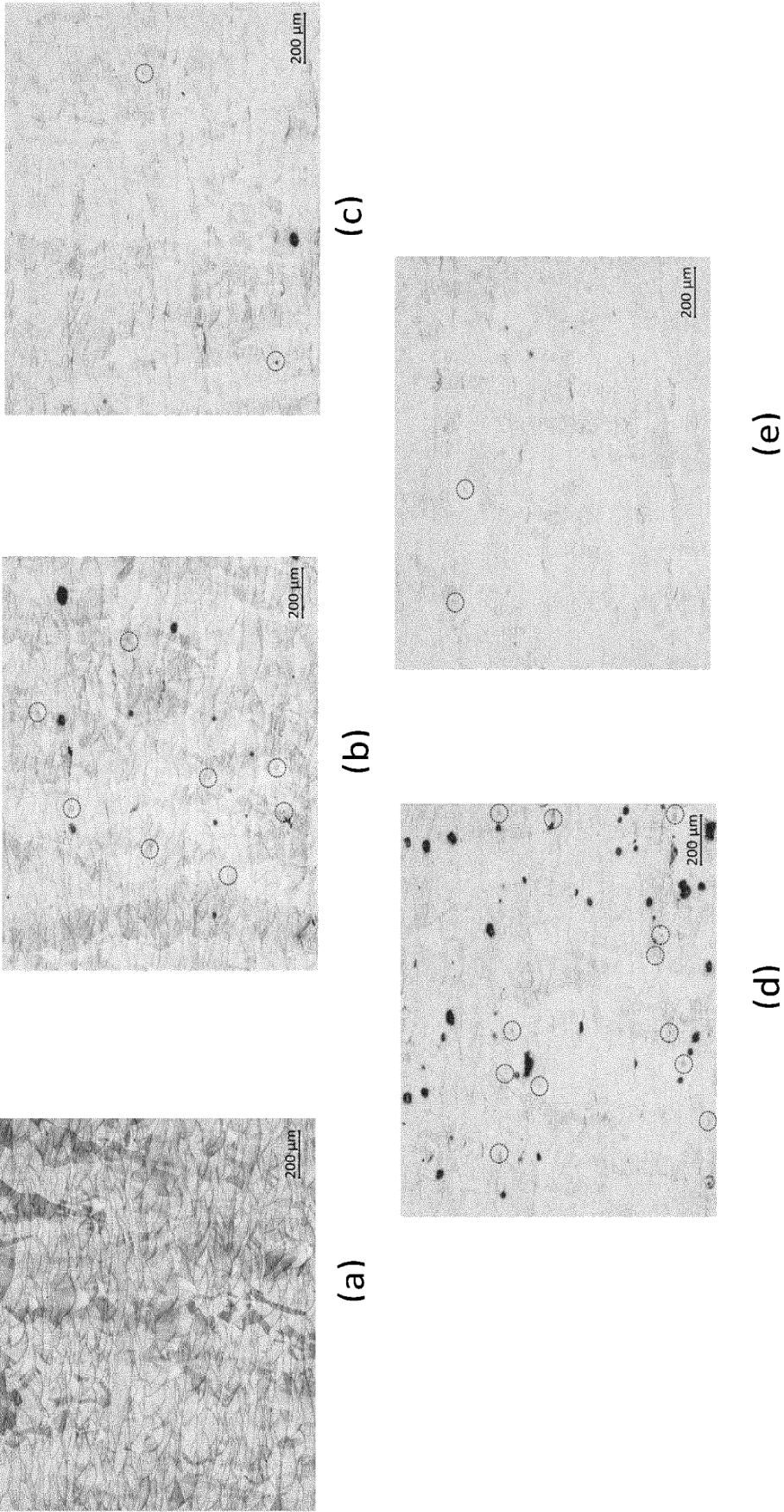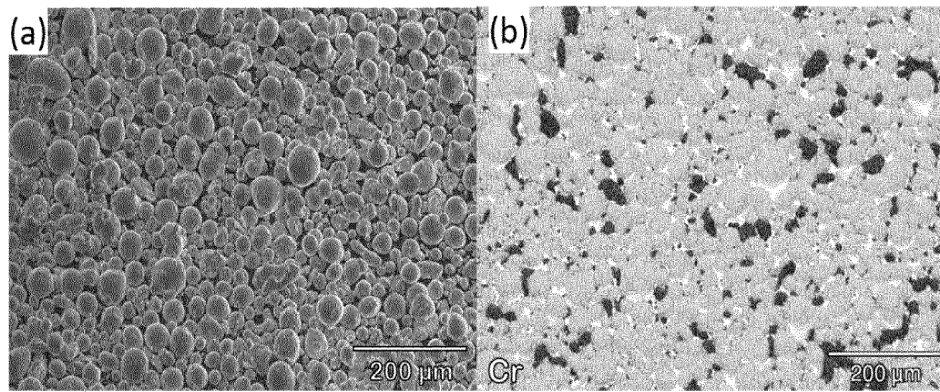
FIGURE 1

FIGURE 2



FIGURE 3

FIGURE 4



FIGURE 5

FIGURE 6



FIGURE 7

316L                                      316L + 2.5wt%Cr₂N                          316L + 2.5wt%Cr₂N + 1wt%Cr₃C₂
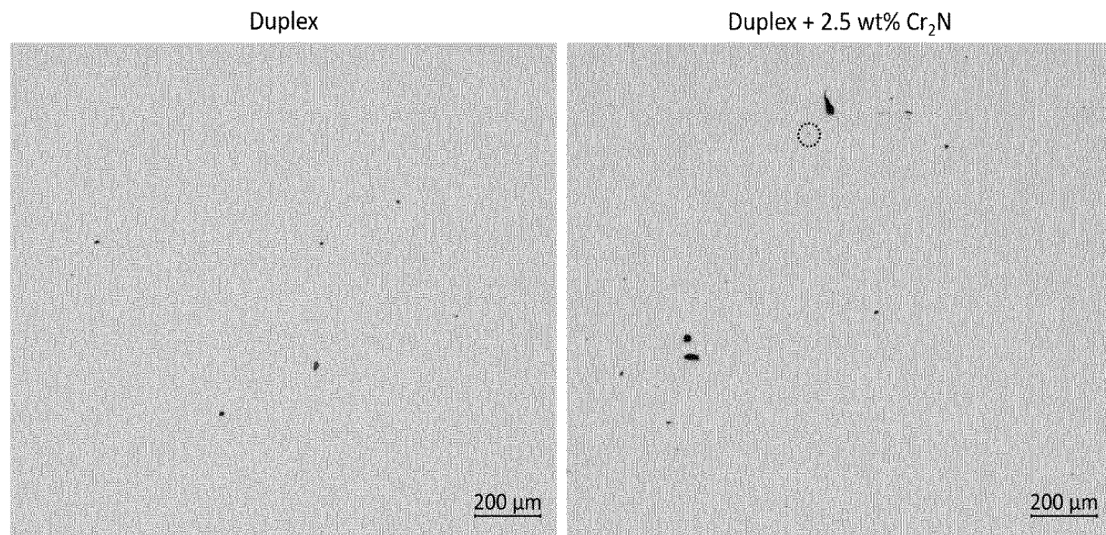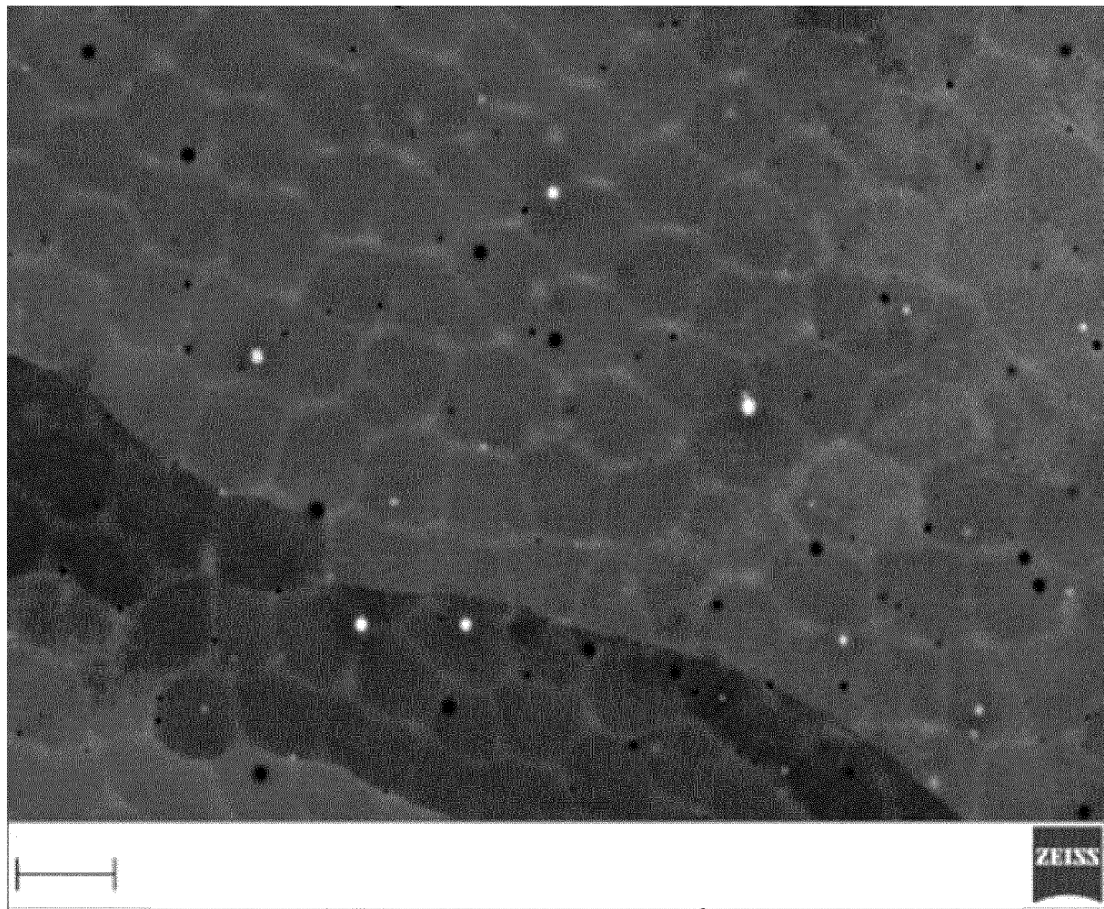


FIGURE 8



FIGURE 9

FIGURE 10
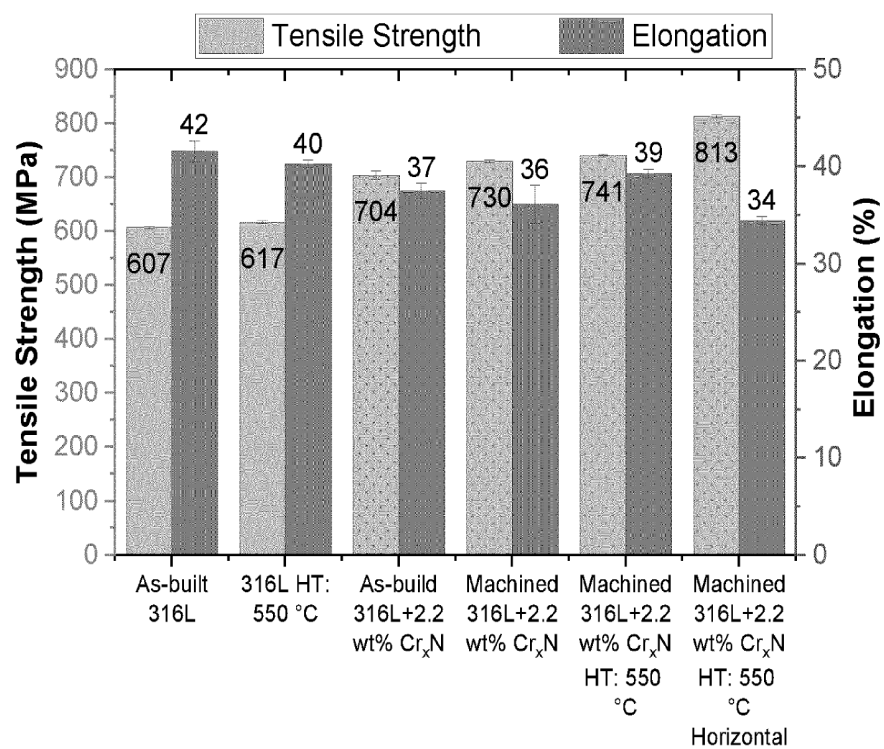


FIGURE 11

FIGURE 12

1 µm
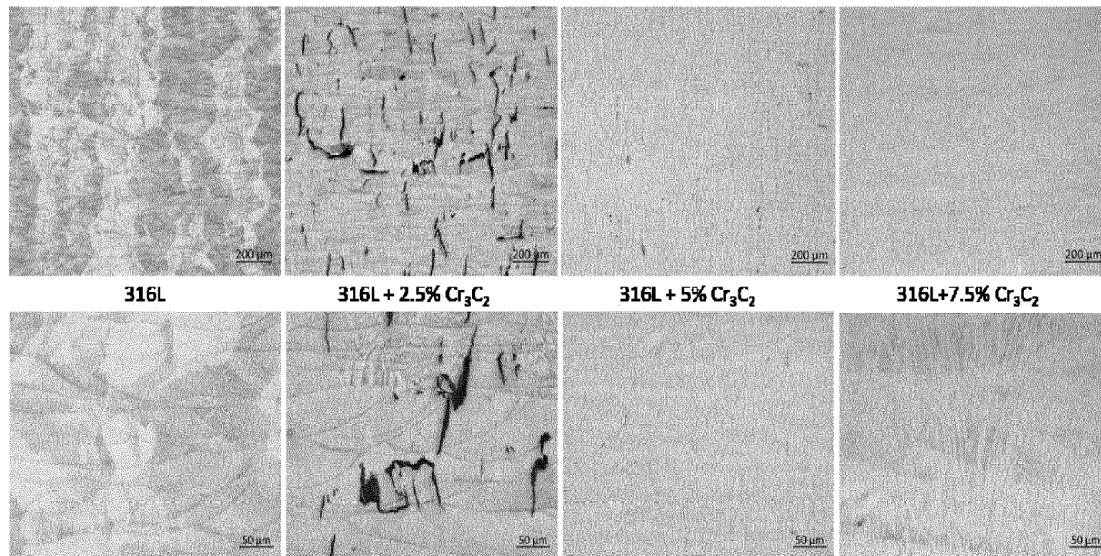
316L

EHT = 15.00V; WD = 5.4 mm; 316Lspecimen3_06.tif; Mag = 10.00 K X; Signal A = BSD1; Aperture Size = 60.00 µm; Width = 11.43 µm; Time 14:18:44; Date: 21 Dec 2021
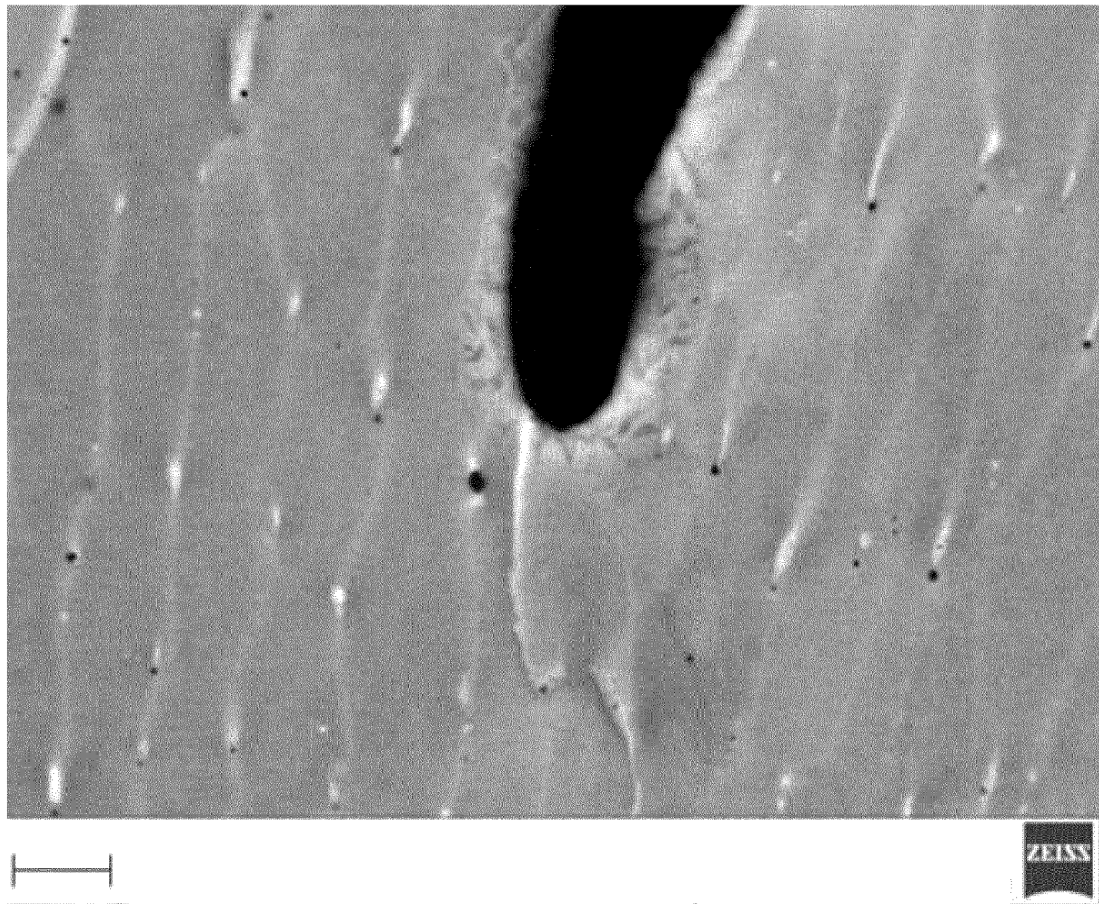
FIGURE 13

10 µm

316L

EHT = 15.00V; WD = 5.4 mm; 316Lspecimen3_03.tif; Mag = 1.00 K X; Signal A = BSD1; Aperture Size = 60.00 µm; Width = 114.3 µm; Time 14:17:52; Date: 21 Dec 2021
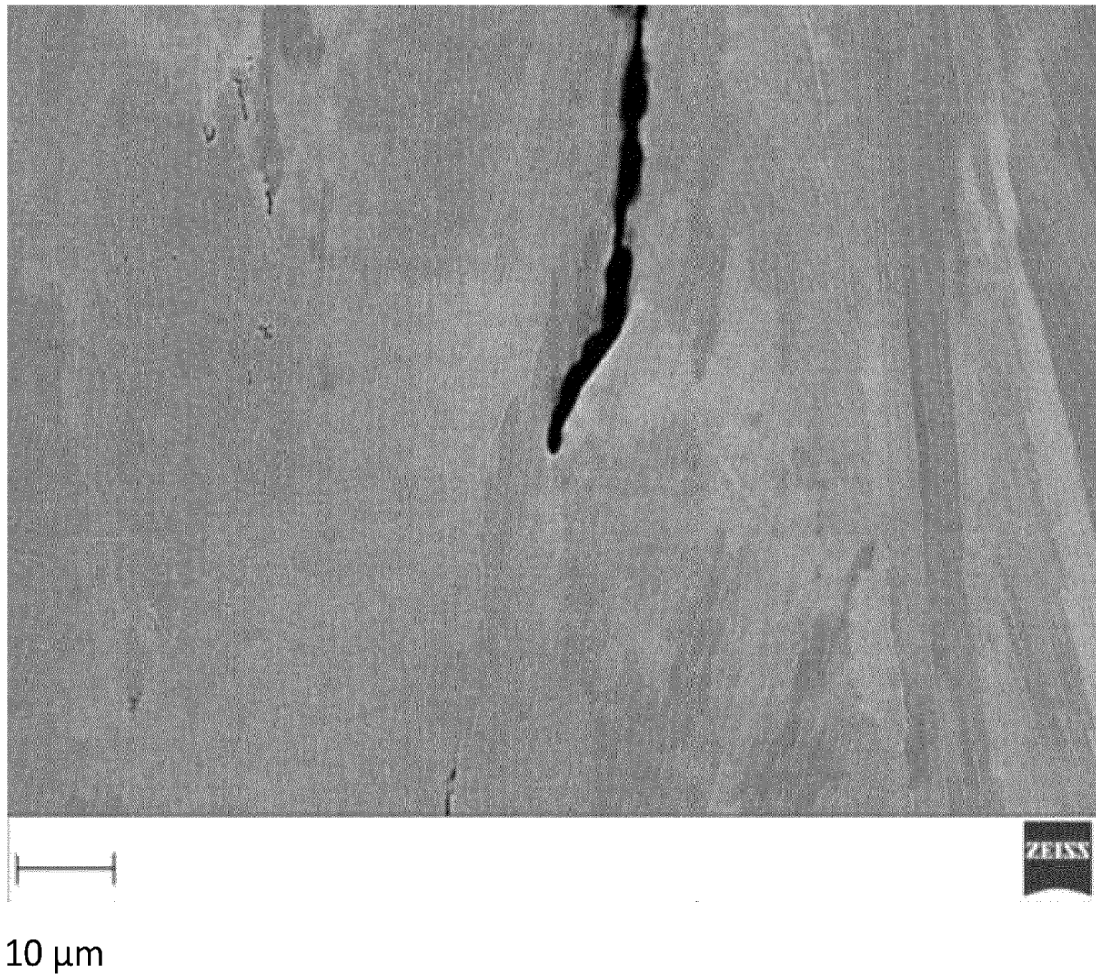
FIGURE 13 (continuation)

SUBSTITUTE SHEET (RULE 26)

1 μm

316L + 2.5% $Cr_3C_2$

EHT = 15.00V; WD = 8.4 mm; 316L25Cr3C2_hog_12.tif; Mag = 10.00 K X; Signal A = BSD1; Aperture Size = 60.00 μm; Width = 11.43 μm; Time 8:56:49; Date: 18 Jan 2022

FIGURE 13 (continuation)

SUBSTITUTE SHEET (RULE 26)

10 µm

$$316L + 2.5\% \; Cr_3C_2$$

EHT = 15.00V; WD = 8.4 mm; 316L25Cr3C2_hog_15.tif; Mag = 1.00 K X; Signal A = BSD1; Aperture Size = 60.00 µm; Width = 114.3 µm; Time 8:59:30; Date: 18 Jan 2022
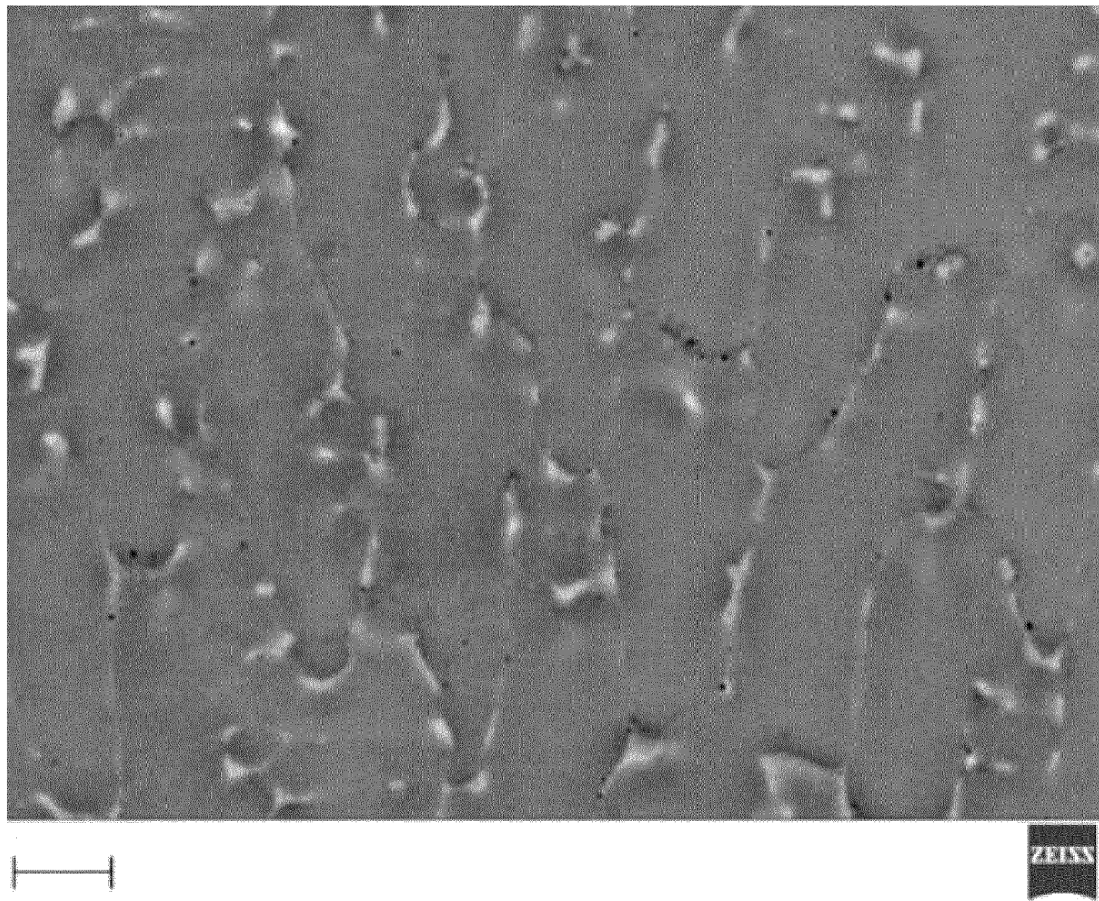
FIGURE 13 (continuation)

1 µm

$$316L + 5\% \ Cr_3C_2$$

EHT = 15.00V; WD = 8.0 mm; 316L5Cr3C2_hog_09.tif; Mag = 10.00 K X; Signal A = BSD1; Aperture Size = 60.00 µm; Width = 11.43 µm; Time 9:16:51; Date: 18 Jan 2022
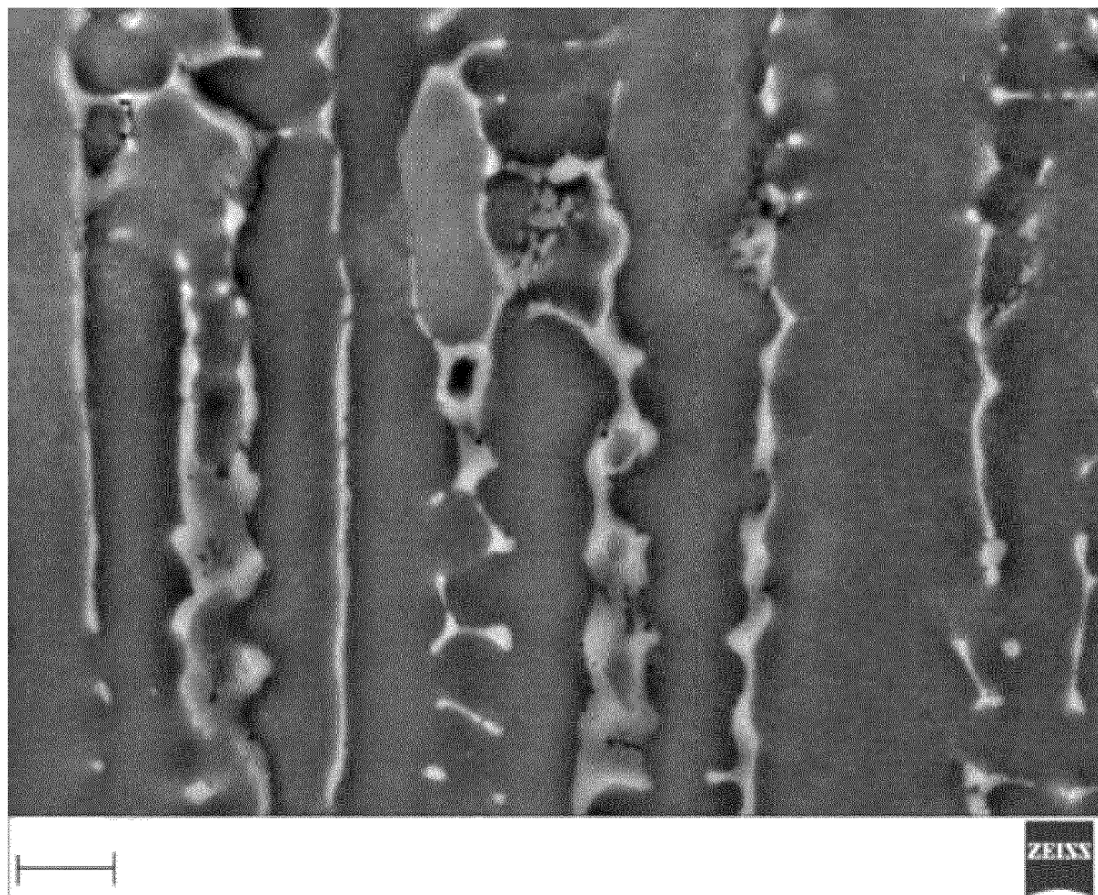
FIGURE 14

10 µm

316L + 5% $Cr_3C_2$

EHT = 15.00V; WD = 8.0 mm; 316L5Cr3C2_hog_12.tif; Mag = 1.00 K X; Signal A = BSD1; Aperture Size = 60.00 µm; Width = 114.3 µm; Time 9:19:04; Date: 18 Jan 2022

FIGURE 14 (continuation)

SUBSTITUTE SHEET (RULE 26)

1 μm

$$316L + 7.5\% \; Cr_3C_2$$

EHT = 15.00V; WD = 8.2 mm; 316L75Cr3C2_hog_03.tif; Mag = 10.00 K X; Signal A = BSD1; Aperture Size = 60.00 μm; Width = 11.43 μm; Time 9:30:27; Date: 18 Jan 2022

FIGURE 14 (continuation)

SUBSTITUTE SHEET (RULE 26)

10 µm

316L + 7.5% Cr$_3$C$_2$

EHT = 15.00V; WD = 8.2 mm; 316L75Cr3C2_hog_06.tif; Mag = 1.00 K X; Signal A = BSD1; Aperture Size = 60.00 µm; Width = 114.3 µm; Time 9:31:59; Date: 18 Jan 2022
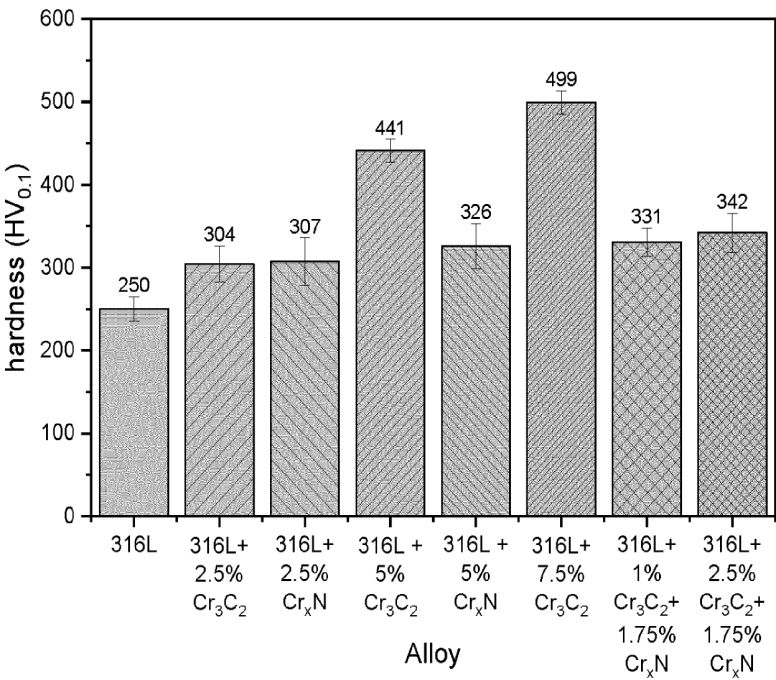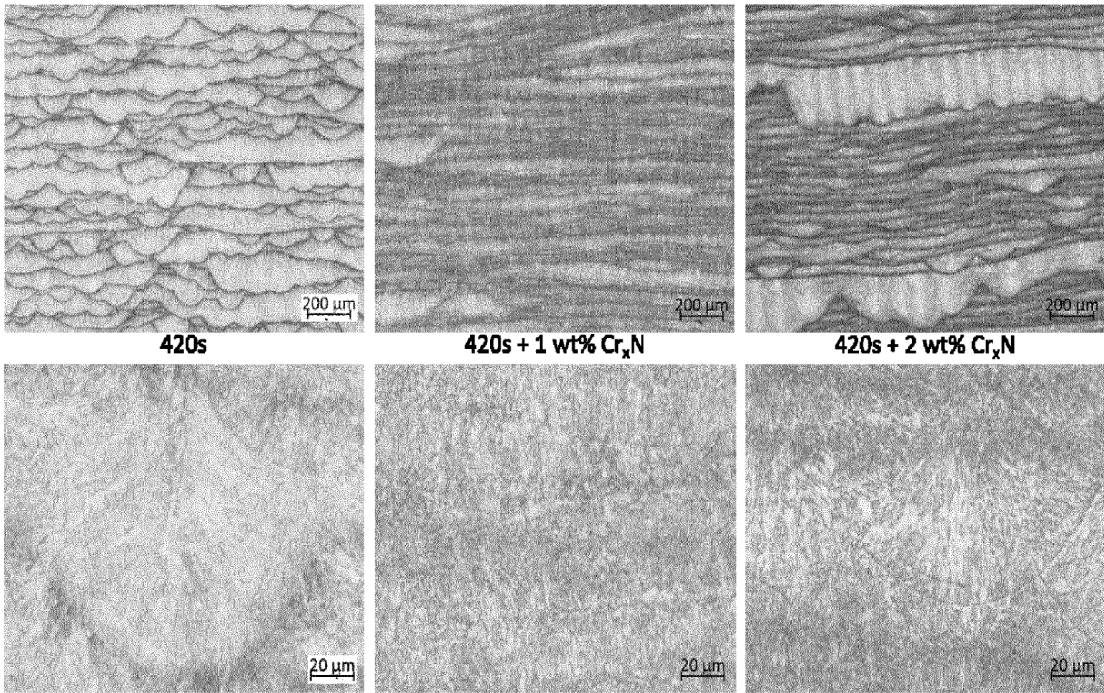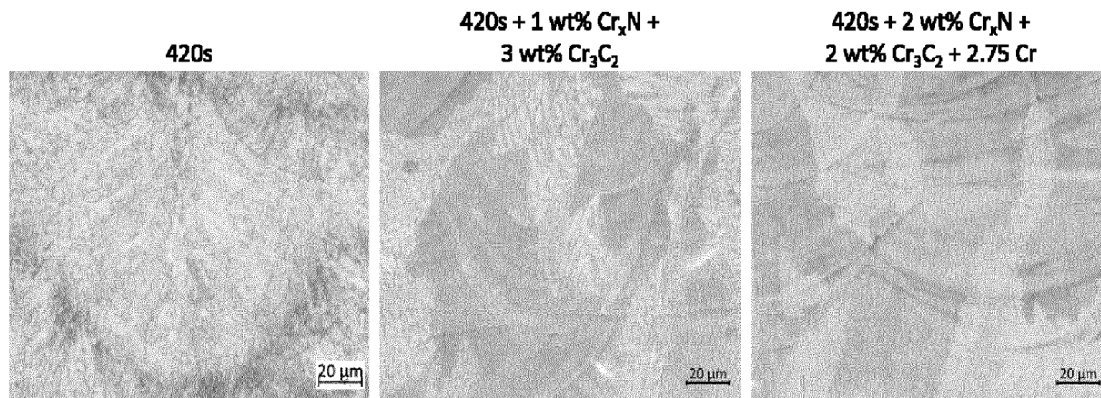
FIGURE 14 (continuation)

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FIGURE 15



FIGURE 16

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420s

420s + 1 wt% Cr$_x$N +
3 wt% Cr$_3$C$_2$

420s + 2 wt% Cr$_x$N +
2 wt% Cr$_3$C$_2$ + 2.75 Cr



FIGURE 17

**A. CLASSIFICATION OF SUBJECT MATTER**

INV.  B33Y10/00    B33Y70/00    C22C19/00    B22F10/20    C22C38/02
      C22C38/04    C22C38/42    C22C38/44    C22C33/02
ADD.  C22C1/04

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)
B33Y  C22C  B22F

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, COMPENDEX, INSPEC, WPI Data

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

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| A | claims | 15 |
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| A | paragraph [0053] | 1-14, 16-22 |
| | ----- | |
| | -/-- | |

| [x] | Further documents are listed in the continuation of Box C. | | [x] | See patent family annex. |
|---|---|---|---|---|

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

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

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

"&" document member of the same patent family

| Date of the actual completion of the international search | Date of mailing of the international search report |
|---|---|
| 31 August 2022 | 08/09/2022 |

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

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