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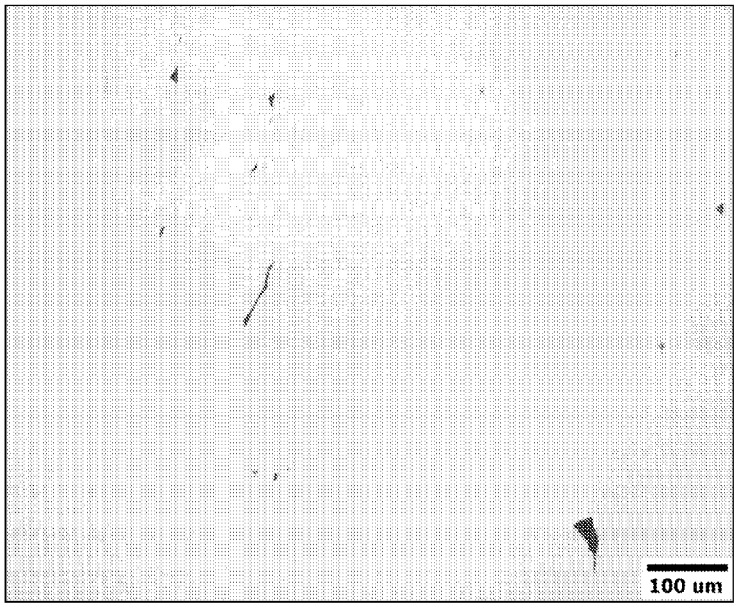


FIG. 1

(57) Abstract: The present invention relates to alloy compositions for 3D metal printing procedures which provide metallic parts with high hardness, tensile strengths, yield strengths, and elongation. The alloys include Fe, Cr and Mo and at least three or more elements selected from C, Ni, Cu, Nb, Si and N. Ni may be replaced with Mn. As built parts indicate a tensile strength of at least 1000 MPa, yield strength of at least 640 MPa, elongation of at least 3.0 % and hardness (HV) of at least 375.

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3D PRINTABLE HARD FERROUS METALLIC ALLOYS FOR POWDER BED FUSION

Cross-Reference to Related Applications

This application claims priority to U.S. Patent Application 16/393,194, filed April 24, 2019, which is a continuation-in-part of U.S. Application 15/800,210, filed November 1, 2017, which claims the benefit of U.S. Provisional Patent Application Serial No. 62/415,667, filed on November 1, 2016, which is fully incorporated herein by reference.

Field

The present disclosure relates to alloy compositions and 3D printing procedures to provide for the formation of metallic parts with relatively high hardness, tensile strengths, yield strengths, and elongation. The alloys also indicate the ability to form desirable phases, such as metal carbide and/or metal carbonitride phases, that contribute to such mechanical property characteristics.

Background

Metal 3D printing processes provide a multitude of exceptional benefits such as the ability to produce highly complex parts with largely reduced part production time. For these reasons 3D printing is of high value to many industries. While many 3D printing processes for building metal parts exist, the most widely adopted processes are those that utilize solid-liquid-solid phase transformations to build parts. These processes are commonly referred to as powder bed fusion (PBF), selective laser melting (SLM), and electron beam melting (EBM), hereinafter these processes are referred to as PBF.

While PBF is exceptionally versatile in its ability to produce complex parts from specific metal alloys, the process has been limited to being able to produce parts from relatively few alloy steels such as 316L, 17-4PH and maraging steel M300. Among these alloys, only M300 has a hardness that is considered sufficient to classify the alloy as a hard alloy (HV>370).

Expanding the material breadth of hard PBF steel alloys has met a variety of issues foremost among which is the occurrence of crack formation upon or after the printing process.

Cracking of parts can be caused by a number of factors such as thermal stresses, hot cracking, and liquation cracking, and generally the potential for cracking increases as the hardness of the built parts increases and the toughness decreases.

Numerous industries have a great deal of interest in utilizing PBF with higher hardness materials (HV> 370) for applications such as tooling, dies, molds, cutting tools, gears, filters, and bearings. In addition to high hardness these applications typically also require high strength, toughness, and corrosion resistance, low environmental health, low safety and stewardship risk, and low cost.

Summary

A method of layer-by-layer construction of a metallic part comprising supplying an iron-based alloy in particle form including the elements Cr and Mo wherein Cr is present at 10.0 wt. % to 19.0 wt. %, Mo is present at 0.5 wt. % to 3.0 wt. % and at least three elements from C, Ni, Cu, Nb, Si and N, wherein C is present at 0 to 0.35 wt. %, Ni is present at 0 to 5.0 wt. %, Cu is present at 0 to 5.0 wt. %, Nb is present at 0 to 1.0 wt. %, Si is present at 0 to 1.0 wt. % and N is present at 0 to 0.25 wt. %;

the balance of said alloy composition containing Fe; and

forming one or more layers of the alloy by melting the alloy into a molten state and cooling and forming a solidified layer of the elements wherein each of the solid layers has a thickness as formed of 2.0 microns to 200.0 microns. The metallic part comprising one or more layers has the following properties: tensile strength of at least 1000 MPa, yield strength of at least 640 MPa, elongation of at least 3.0%, hardness (HV) of at least 375. In the above composition, Mn may replace Ni. Mn may therefore be present to replace Ni and be present at a level of greater than 0 wt. % up to and including 5.0 wt. %.

The present invention also relates to a 3D printed metallic part comprising one or more iron based metallic alloy layers including the elements Cr and Mo wherein Cr is present at 10.0 wt. % to 19.0 wt. %, Mo is present at 0.5 wt. % to 3.0 wt. % and at least three elements from C, Ni, Cu, Nb, Si and N, wherein C is present at 0 to 0.35 wt. %, Ni is present at 0 to 5.0 wt. %, Cu

is present at 0 to 5.0 wt. %, Nb is present at 0 to 1.0 wt. %, Si is present at 0 to 1.0 wt. % and N is present at 0 to 0.25 wt. % and the balance of said alloy composition contains Fe;

said layers having thickness in the range of 2.0 microns to 200.0 microns; and

said printed metallic part indicates a tensile strength of at least 1000 MPa, yield strength of at least 640 MPa, elongation of at least 3.0%, and hardness (HV) of at least 375. In the above composition, Mn may again replace Ni.

The present invention also relates to a method of layer-by-layer construction of a metallic part comprising:

supplying an iron-based alloy in particle form comprising Fe at 82.0 wt. % to 86.0 wt. %; Cr at 10.5 to 12.0 wt.%; Ni at 1.5 to 2.5 wt. %; Mo at 0.8 wt. %. to 1.1 wt. %, C at 0.14 to 0.19 wt. %, Nb at 0.02 to 0.06 wt. %, N at 0.04 to 0.09 wt. % and Si at 0.25 wt.% to 0.75 wt. %; and

forming one or more layers of the alloy by melting the alloy into a molten state and cooling and forming a solidified layer of the elements wherein each of the solid layers has a thickness as formed of 2.0 microns to 200.0 microns;

said metallic part having the following properties: tensile strength of at least 1000 MPa, yield strength of at least 640 MPa, elongation of at least 3.0%, hardness (HV) of at least 375.

The present invention also relates to: a method of layer-by-layer construction of a metallic part comprising:

supplying particles of an iron-based alloy, the iron-based alloy comprising:

Cr in an amount ranging from 10.0 wt. % to 19.0 wt. %;

Mo in an amount ranging from 0.5 wt. % to 3.0 wt. %;

at least three elements from C, Mn, Cu, Nb, Si and N; and

the balance of said iron-based alloy containing Fe; and

forming an as-built metallic part by powder bed fusing, said powder bed fusing comprising melting the particles into a molten state and cooling and forming one or more solidified layers of the iron-based alloy; wherein

wherein one of the at least three elements is Mn, which is present in the iron-based alloy in an amount ranging from greater than 0 to less than or equal to 5.0 wt. %;

when C is in the iron-based alloy, it is present in an amount of 0.35 wt. % or less;

when Cu is in the iron-based alloy, it is present in an amount of 5.0 wt. % or less;

when Nb is in the iron-based alloy, it is present in an amount of 1.0 wt. % or less;

when Si is in the iron-based alloy, it is present in an amount of 1.0 wt. % or less; and

when N is in the iron-based alloy, it is present in an amount of 0.25 wt. % or less;

each of the one or more solidified layers has an as-formed thickness of 2.0 microns to 200.0 microns; and

said as-built metallic part has a tensile strength of at least 1000 MPa, a yield strength of at least 640 MPa, an elongation of at least 3.0%, and a hardness (HV) of at least 375.

Brief Description of the Figures

FIG. 1 is an optical image of alloy 1 (A10) built on a SLM 280 HL machine.

FIG. 2 is an optical image of alloy 1 (A10) built on a Trumpf TRUMAFORM LF 250 PBF machine.

FIG. 3 is an optical image of alloy 1 (A10) built on an EOS machine with a density >99.5%.

FIG. 4 shows a 10,000x SEM micrograph of as-built alloy 1 (A10).

FIG. 5 shows the alloy 1 equilibrium phase diagram produced with Thermo-Calc.

FIG. 6 shows microstructures at the surface of a part made of alloy 5 (Table 1) at two different magnifications after carburization.

FIG. 7 shows hardness as a function of depth in a carburized case hardened alloy 5 and alloy 8 (Table 1).

FIG. 8 shows microstructures at the surface of a part of alloy 9 (Table 1) at two different magnifications after nitriding.

FIG. 9 shows hardness as a function of depth in a nitrided case hardened alloy 8 and 9 (Table 1).

Detailed Description

A new class of steel alloys have been developed that combine excellent printability with, in both the "as built" and in the "heat treated" state, high hardness (> 375 HV), high yield and tensile strength, and high elongation as well as low safety (EH&S) and stewardship risk and relatively low cost.

Printability of an alloy is defined as the ease of printing a metal alloy on a variety of commercial PBF machines without cracking or excessive porosity in the built parts. The as-built condition is understood herein as the condition of the PBF built parts upon removal from the PBF machine, i.e. without any post-build heat treatment. The heat treated condition is understood herein as the condition of the PBF built parts that have been subjected to a post-build heat treatment. The alloys herein are capable of 3D printing which refers to a process to create a three-dimensional object.

Table 1 below sets out the alloy chemistries that are preferably employed herein, which includes alloy 1 (A10) and then 10 additional alloys for a total of 11 alloys:

Table 1 – Alloy Chemistries (Wt. %)

Alloy	Fe	C	Cr	Ni	Cu	Nb	Mo	Si	N	Mn
1 (A10)	84.93	0.16	10.64	1.96	0.54	0.03	1.48	0.19	0.07	0
2	84.92	0.25	11.5	1	0.5	0.03	1.5	0.25	0.05	0
3	84.97	0.2	11.5	1	0.5	0.03	1.5	0.25	0.05	0
4	84.96	0.16	11.5	1.05	0.59	0.04	1.51	0.18	0	0
5	84.57	0.21	11.21	1.93	0.12	0.03	1.7	0.19	0.04	0
6	81.66	0.21	15.55	0.88	0.55	0.03	0.89	0.16	0.07	0
7	82.82	0.21	11.69	0.94	2.56	0.06	1.47	0.17	0.08	0
8	86.85	0.1	10.56	0	0.56	0.04	1.61	0.14	0.14	0
9	85.37	0.17	11.01	1.85	0	0.04	0.95	0.53	0.074	0
10	86.64	0.12	10.55	0	0.55	0.08	1.52	0.39	0.14	0
11	87.03	0.11	11.03	0	0	0.08	1.38	0.2	0.16	0
12	84.19	0.23	10.6	0	0.69	0.04	1.99	0.39	0.133	1.74

Accordingly, it can be appreciated from the above that one supplies a metal alloy in particle form comprising, consisting essentially of, or consisting of Fe, Cr and Mo, wherein Cr is present at 10.0 wt. % to 19.0 wt. %, Mo is present at 0.5 wt. % to 3.0 wt. % and at least three or more elements from C, Ni, Cu, Nb, Si and N, wherein C is present at 0 to 0.35 wt. %, Ni is present at 0 to 5.0 wt. %, Cu is present at 0 to 5.0 wt. %, Nb is present at 0 to 1.0 wt. %, Si is present at 0 to 1.0 wt. % and N is present at 0 to 0.25 wt. %. The balance of said alloy composition contains Fe. Accordingly, one may select four elements, five elements or all six elements from C, Ni, Cu, Nb, Si and N for a given alloy formulation. Mn may also replace Ni and be present at a level of greater than 0 wt. % to 5.0 wt. %.

In a preferred embodiment, one again supplies a metal alloy in particle form comprising, consisting essentially of, or consisting of Fe, Cr and Mo, wherein Cr is present at 10.0 wt. % to 18.3 wt. %, Mo is present at 0.5 wt. % to 2.5 wt. % and at least three or more elements from C, Ni, Cu, Nb, Si and N, wherein C is present at 0 to 0.30 wt. %, Ni is present at 0 to 4.0 wt. %, Cu is present at 0 to 4.0 wt. %, Nb is present at 0 to 0.7 wt. %, Si is present at 0 to 0.7 wt. % and N is present at 0 to 0.25 wt. %. The balance of said alloy composition contains Fe.

Furthermore, the alloy may include some amount of inevitable impurities wherein the level of such impurities may be up to 1.0 wt. %, for example, an element not listed above may also be present at a level of up to 1.0 wt. %, where the corresponding level of Fe can then be reduced 1.0

wt. %. With regards to impurities, it is noted that such is contemplated to include elements such as sulfur, phosphorous and oxygen.

Alloy 1, which was previously designated as alloy A10, may itself have the following preferred composition: Fe at 82.0 to 86.0 wt. %; Cr at 10.5 to 12.0 wt.%; Ni at 1.5 to 2.5 wt. %; Cu at 0.4 to 0.7 wt. %; Mo at 1.2 to 1.8 wt. %, C at 0.14 to 0.18 wt. %, Nb at 0.02 to 0.05 wt. %, N at 0.04 to 0.07 wt. % and Si at 0 – 1.0 wt. %.

In addition to the above, it has also been found that with respect to the use of any Ni in the aforementioned alloys, which as noted may be present at a level of 0 to 5.0 wt. %, one may replace the presence of any such Ni with Mn at 0 to 5.0 wt. %. Accordingly, the metal alloy herein in particle form may also comprise, consist essentially of, or consist of Fe, Cr. Mo, wherein Cr is present at 10.0 wt. % to 19.0 wt. %, Mo is present at 0.5 wt. % to 3.0 wt. %, and at least three or more elements from C, Mn, Cu, Nb, Si and N, where C is present at 0 to 5.0 wt. %, Mn is present at 0 to 5.0 wt. %, Cu is present at 0 to 5.0 wt. %, Nb is present at 0 to 1.0 wt. %, Si is present at 0 to 1.0 wt. % and N is present at 0 to 0.25 wt. %. Accordingly, one may again select four elements, five elements or all size elements from C, Mn, Cu, Nb, Si and N. More preferably, the level of Mn may be in the range of up to 4.0 wt.%, or up to 3.0 wt. %, or in the range of up to 2.0 wt. %. Even more preferably, the level of Mn may be in the range of 0.1 wt % to 2.0 wt. %.

In addition, it has also been found that alloy 9 in the above referenced Table 1 has particular utility herein. Accordingly, it is further contemplated that one may utilize herein a metal alloy in particle form, comprising, consisting essentially of, or consisting of Fe at 82.0 wt. % to 86.0 wt. %; Cr at 10.5 to 12.0 wt.%; Ni at 1.5 to 2.5 wt. %; Mo at 0.8 wt. %. to 1.1 wt. %, C at 0.14 to 0.19 wt. %, Nb at 0.02 to 0.06 wt. %, N at 0.04 to 0.09 wt. % and Si at 0.25 wt.% – 0.75 wt. %. As can be seen, such alloy preferably does not contain any Cu or Mn.

The metal alloy is supplied to the PBF process in powder particle or wire form and is preferably produced using conventional melting with either gas, centrifugal, atomization utilizing gases such as nitrogen or argon gas, or water atomization. Nitrogen gas melting and atomization can be used to increase the nitrogen content in the powder alloy. The powder particles can have a diameter in the range of 1 to 200 microns, more preferably from 3 to 70 microns, and most preferably from 15 to 53 microns.

PBF parts are preferably built from the metal alloy herein using commercially available conventional PBF machines such as the SLM®280HL or EOS M-280 and a Trumpf TRUMAFORM LF 250. The parts are preferably built in a nitrogen or argon atmosphere. Parts may be built on a metal substrate that is preheated up to 300°C, such as in the range of 100°C to 300°C, and more preferably in the range of 20°C to 200°C. In addition, no preheating of the substrate can be employed. For the PBF procedure herein one may utilize one or a plurality of lasers or electron beams with an energy density of 30 to 500 J/m^3, more preferably in the range of 50 J/mm^3 to 300 J/m^3 and most preferably in the range of 60 J/mm^3 to 200 J/mm^3.

The metal substrate is preferably composed of the alloys 1-11 in **Table 1** or from other materials e.g. from type 304L stainless steel. The PBF procedure herein contemplates a build-up of individual layers each having a thickness typically in the range of 2.0 microns to 200.0 microns, more preferably 5.0 microns to 150.0 microns, and most preferably 5.0 microns to 120.0 microns. Accordingly, a suitable range of thickness for the built-up layers is 2.0 microns and higher. More commonly, however, the thickness range for the built up layers (combination of individual layers) is from 2 microns to 800 mm and even higher depending upon the capability or requirements of a given printing procedure.

Porosity and cracking in parts can negatively affect a number of part properties including strength, toughness, and fatigue resistance. As such, it is desired for dense parts to minimize porosity and cracking in PBF parts. Porosity in parts is preferably less than 1.0%, more preferably less than 0.5%, and most preferably less than 0.2% although some large parts can tolerate higher porosity levels, such as a porosity of greater than 1.0% to 15.0%. Low porosity and no cracking in the as-built PBF parts with the metal alloys herein is evidenced in the cross-sectional optical micrograph images shown in **FIGS. 1-3** which were taken from parts built with alloy 1 (A10) on SLM 280HL and Trumpf TRUMAFORM LF 250 PBF machines, and an EOS M280/290, respectively. The parts shown in **FIGS. 1-3** were built on a substrate with no preheating to a height of 10 mm, using 0.040 mm thick layers, for a total of 250 layers in the parts. Porosity is measured with optical image analysis at 100X magnification and alloy 1 show porosity of less than 0.2%.

PBF parts are preferably heat treated after the parts are built to be able to achieve relatively high hardness, strength, and ductility. Achieving high hardness in-situ with building parts without cracking is relatively difficult due to the thermal stresses and thermal fatigue in the parts as they

are built, combined with the typically low toughness and ductility of high hardness alloys. PBF uses an energy source to create a small, quickly traversing, molten metal weld pool to selectively melt the powder in a powder layer, which then re-solidifies adding the next layer in the part. The heat of the traversing weld pool is largely conducted into the part, which results in raising the overall part temperature and providing relatively large temperature gradients in the local vicinity of the weld pool. Large continuous and cyclic thermal stresses can arise in parts during PBF part building due to the thermal gradients and phase transformations in the parts. Parts therefore preferably have sufficient strength, toughness, and ductility to resist crack formation under the localized stress conditions and resist crack propagation under the continuous and cyclic stresses.

"As-Built" alloy properties: **Table 2** shows comparative mechanical properties of PBF parts produced with commercial PBF steel alloys and alloy 1 (A10) from **Table 1** in the as-built condition (without a post-heat treatment). Properties of alloy 1 (A10) were measured on parts that were PBF built on a substrate with no preheating to a height of 10 mm, using 0.040 mm thick layers, for a total of 250 layers in the parts. **Table 2** shows the increased hardness and strength of the metal alloy herein over the commercially applied crack-free steel alloys.

Table 2

Alloy	Tensile Strength [MPa]	Yield Strength [MPa]	Elongation [%]	Hardness [HV]
316L	640	530	40	171
17-4PH	930	586	25	230
M300	1100	1050	10	332
Alloy 1 (A10)	1504	1254	17	454

With respect to the hardness data in **Table 2**, it is worth noting that the reported hardness is such that it is observed to be a function of the alloy composition as well as the printing procedure employed. Accordingly, in the case of, e.g. M300, the printing hardness may vary, depending upon the printing procedure, such that the HV hardness may be in the range of 320 to 370.

Table 3 below now provides the mechanical properties for all the alloys identified in **Table 1** in the "AB" or as-built condition, without a heat treatment and in condition "B1" which is reference to a heat treatment, which heat treatment is discussed further herein:

Table 3

Alloy	Test Condition	Hard. (HV)	YS (MPa)	UTS (MPa)	Elong. (%)
1 (A10)	**AB**	454	1254	1504	17
	B1	502	1325	1659	16
4	**AB**	450	1048	1082	3
	B1	491	995	1011	1
5	**AB**	531	1207	1659	19
	B1	556	1338	1785	10
6	**AB**	381	649	1422	19
	B1	519	1329	1631	12
7	**AB**	415	1003	1538	20
	B1	574	1571	1880	6
8	**AB**	455	1041	1274	8
	B1	561	1345	1629	13
9	**AB**	474	1274	1552	15
	B1	531	1337	1676	14
10	**AB**	438	979	1191	7
	B1	564	1368	1637	10
11	**AB**	501	1090	1365	7
	B1	563	1438	1621	5

As may therefore be appreciated from the above, the alloys herein, in the as-built condition (no heat treatment) are such that they indicate a tensile strength of at least 1000 MPa, more preferably at least 1100 MPa, or at least 1200 MPa, and even more preferably, at least 1300 MPa. Moreover, it can now be appreciated that the tensile strength of the as built alloys herein falls in the range of 1000 MPa to 1900 MPa, or 1100 MPa to 1900 MPa, or 1200 MPa to 1900 MPa or 1300 MPa to 1900 MPa.

The above tensile strength is achieved in combination with a yield strength of at least 640 MPa, or at least 700 MPa, or at least 800 MPa, or at least 900 MPa, or at least 1000 MPa, or at least 1100 MPa, or at least 1200 MPa, or at least 1300 MPa, or at least 1400 MPa or at least 1500

MPa. Moreover, it can now be appreciated that the yield strength of the as built alloys herein falls in the range of 640 MPa to 1500 MPa.

Moreover, the above tensile strength and yield strength is also preferably achieved in combination with an elongation of at least 3%, 4%, 5%, 6%, 7%, 8%, 9%, 10%, 11%, etc. up to 25%. Moreover, it can be appreciated that the elongation of the as built alloys herein fall in the range of 3% to 25%.

The above tensile strength, yield strength and elongation is then preferably achieved in combination with a hardness (HV) value of at least 375, 400, 410, 420, 430, 440, etc. up to 600. Moreover, it can be appreciated that the HV values of the alloys herein fall in the range of 375 to 600. It is worth noting that alloy 12 herein indicated an HV value of 420-600.

Accordingly, it should be appreciated that the alloys herein are such that they can provide in the as built condition a tensile strength of at least 1000 MPa, a yield strength of at least 640 MPa, and elongation of at least 3% and a hardness (HV) value of at least 375. Other combinations of tensile strength, yield strength, elongation and hardness may now be selected from the individual preferred levels of tensile strength, yield strength, elongation and hardness noted herein for the non-heat treated alloy.

FIG. 4 shows a 10,000X, secondary electron, scanning electron microscopy (SEM) micrograph of a PBF-produced, as-built, alloy 1 (A10) part. The part shown in **FIG 4** was built on a substrate with no preheating to a height of 10 mm, using 0.040 mm thick layers, for a total of 250 layers in the parts. SEM imaging was performed on a Jeol JSM-7001F Field Emission SEM. The microstructure in **FIG. 4** is contemplated to contain the BCC/martensite, FCC, M_2CN, and M_7C_3.

FIG. 5 shows the alloy 1 (A10) equilibrium phase diagram produced with Thermo-Calc showing the phase fraction of each phase that is thermodynamically stable over a temperature range from 20°C to 1500°C. The equilibrium phase diagram was used to identify the phases with the highest potential to contribute to increasing hardness and strength.

It is contemplated that the elevated temperature of PBF parts during building, which is caused by heat transfer to the part from the traversing weld pool, may be sufficiently high in the

metal alloys herein to drive in-situ precipitation of secondary phases such as the Cu-rich FCC phase, the M_2N ($(Cr,Mo)_2N$) phase, and the $M_{23}C_6$ ($(Cr,Fe,Mo)_{23}C_6$) phase shown in the **FIG. 5** phase diagram for alloy 1 (A10). The in-situ precipitation of these phases during the part build is expected to contribute to the part strength and hardness in the as-built condition.

"Heat Treatment": PBF parts produced with the metal alloys herein can be further enhanced by heat treating to increase the strength and hardness of the parts. It is contemplated that various heat treatments can be performed to affect the part properties and the heat treatment temperatures can be selected from equilibrium phase diagrams.

Effective heat treatments for the metal alloys herein are contemplated to include (1) high temperature solutionizing (dissolving one or more of the secondary phases), quenching, and tempering (precipitation of the secondary phases) and/or (2) tempering of the as-built part, with each heat treating step being performed in a vacuum, argon, or nitrogen atmosphere. Solutionizing is preferably performed at a temperature of greater than 900°C, and for example in the range of 900 °C to 1400 °C and tempering is preferably performed at a temperature in the range of 150-900°C.

(1) The high temperature solutionizing and quenching step is contemplated to:
   a. reduce anisotropy in the part that can result from the PBF process,
   b. increase martensite content and thereby hardness and possibly strength
   c. dissolve Cr carbides and/or Cr nitrides that can negatively affect the corrosion resistance of the part,
   d. coarsen the undissolved carbides and/or nitrides.

(2) Further strengthening and hardening of the part via additional precipitation of various phases is contemplated to be initiated by subsequent tempering treatments.

"Heat Treatment" - procedure: The equilibrium phase diagram in **FIG. 5** was used to select solutionizing and tempering temperatures for PBF parts from alloy 1 (A10). The heat treatment used on the alloy 1 (A10) PBF parts consisted of solutionizing at 1000°C for 1.5 hr followed by a gas quench to -84°C for 2 hours, and finally tempering at 454°C for 48 hr in Argon to strengthen and harden the part.

"Heat Treated" – alloy properties: Properties of the heat treated PBF alloy 1 (A10) parts are shown in **Table 4** along with commercial PBF steel alloys after subjecting them to their manufacturer-prescribed heat treatments for PBF parts. Properties of heat treated alloys 1, 4, 5, 6, 7, 9, 0, 10 and 11 were also listed in **Table 3**. Properties of alloy 1 (A10) were measured on heat treated parts that were PBF built on a substrate with no preheating to a height of 10 mm, using 0.040 mm thick layers, for a total of 250 layers in the parts. The hardness of alloy 1 (A10) shown in **Table 4** was taken at the surface of the heat treated part.

Table 4

Alloy	Tensile Strength [MPa]	Yield Strength [MPa]	Elongation [%]	Hardness [HV]
316L	843	587	28	262
17-4PH	1100	590	29	311
M300	2050	1990	2	544
Alloy 1 (A10)	1659	1325	16	502

As may therefore be appreciated from **Tables 3** and **4**, the alloys herein following heat treatment are such that they indicate a tensile strength of at least 1000 MPa, or at least 1100 MPa, or at least 1200 MPa, or at least 1300 MPa, or at least 1400 MPa, or at least 1500 MPa, or at least 1600 MPa, or at least 1700 MPa, or at least 1800 MPa. Moreover, it can be appreciated that the heat-treated alloys have a tensile strength in the range of 1000 MPa to 1900 MPa.

Such tensile strength is achieved in combination with a yield strength of at least 900 MPa, or at least or at least 1000 MPa, or at least 1100 MPa, or at least 1200 MPa, or at least 1300 MPa, or at least 1400 MPa, or at least 1500 MPa, or at least 1600 MPa. Moreover, it can be appreciated that the heat-treated alloys herein have a yield strength in the range of 900 MPa to 1600 MPa.

Such tensile strength and yield strength is also preferably achieved in combination with an elongation of at least 1%, 2%, 3%, 4%, 5%, 6%, 7%, 8%, 9%, 10%, etc. up to 16%. Moreover, it can be appreciated that the heat-treated alloys herein have elongation values in the range of 1% to 16%.

Such tensile strength, yield strength and elongation is then preferably achieved in combination with a hardness (HV) value of at least at least 475, or at least 500, or at least 525, or at least 550, or at least 600. Moreover, it can be appreciated that the heat-treated alloys herein have HV values in the range of 475 to 650.

Accordingly, it should be appreciated that the alloys herein with heat treatment are such that they can provide, e.g., a tensile strength of at least 1000 MPa, a yield strength of at least 900 MPa, and elongation of at least 1% and a hardness (HV) value of at least 475. Other combinations of tensile strength, yield strength, elongation and hardness may now be selected from the individual preferred levels of tensile strength, yield strength, elongation and hardness noted herein for the heat treated alloy.

Table 4 shows that heat treatment does not raise the hardness of 316L and 17-4PH to a level that either alloy could be classified as a hard alloy (HV>370). Only the hardness value of M-300 after heat treatment classifies the alloy as a hard alloy (HV>370) and M300 is currently the primary alloy choice in additive manufacturing when a hard alloy is required. However, the application space of M-300 is highly limited since M300 features at such hardness levels indicate only a low elongation (2%), indicating a tendency for parts to fracture or undergo chipping when exposed to even small impact force such as dropping the part to the floor. Therefore, the application of M300 finds relatively limited industrial use. Additionally, the M300 alloy contains a significant concentration of relatively high cost elements (18 wt% Ni, 9 wt% Co, and 5 wt% Mo) and as such would not be considered a low-cost alloy further limiting its industrial use. Finally, the industrial use of M-300 is further limited due to its potential EH&S and product stewardship risks given its high cobalt content. Cobalt is known to be a health risk upon inhalation and a stewardship risk due to its classification as a conflict mineral since it is mainly sourced from the Republic of Congo.

In contrast, the heat-treated alloy 1 (A10) has numerous benefits compared to the current incumbent M300. Alloy 1 (A10) has a higher hardness, a higher elongation, a lower cost structure, and is preferably cobalt free.

Case Hardening Treatment - The surface hardness of PBF parts produced with the metal alloys herein can be further enhanced by carburizing and nitriding case hardening treatments. These treatments introduce carbon and nitrogen, respectively, to the surface of the part, creating a case layer with increased hardness relative to the "as-built" or "heat-treated" conditions while retaining the heat treated properties in the core. It is contemplated that other treatments employed for case hardening such as carbonitriding can also be used.

Carburizing – The carburizing process for the metal alloys herein preferably includes a combination of the following steps: oxide reduction, carburizing, solutionizing, quenching, and tempering. Oxide reduction is performed in a reducing atmosphere at temperatures preferably between 800 °C and 1200 °C, more preferably between 900 °C and 1150 °C, and most preferably between 950 °C and 1100 °C. Carburizing is performed by a method that provides or generates a source of carbon in the atmosphere or environment surrounding the part, such as pack, gas, vacuum, liquid, and plasma carburizing, at temperatures preferably between 800 °C and 1000 °C, more preferably between 850 °C and 975 °C, and most preferably between 875 °C and 950 °C.

The carburization results in an enrichment of carbon at the surface of the part resulting in a layer of material with a different microstructure compared to that of the core as seen at two different magnifications in FIG. 6 for alloy 5. This structure results in a maximum hardness at the exterior surface that is preferably 650 to 1000 HV, more preferably 700 to 975 HV, and most preferably 800 to 950 HV. The hardness then progressively decreases with increasing distance from the exterior surface (i.e. depth into the part) until it reaches a steady-state value in the core similar to heat treated values discussed herein. Representative examples of the hardness as a function of depth in carburized case hardened alloys 5 and 8 are seen in **FIG. 7**. Other alloys listed herein can similarly be case hardening by a carburizing process with similar effectiveness. The level of carbon can be increased at the surface down to a depth of at least 2.0 mm, and up to 4.0 mm.

Nitriding – The nitriding process for the metal alloys herein includes a combination of the following steps: solutionizing, quenching, and tempering. It is contemplated that the nitrogen may be introduced to the surface of the part by other nitriding methods, including plasma and liquid nitriding processes. The enrichment of nitrogen at the surface of the part results in a layer of material with a different microstructure compared to that of the core as seen at two different magnificiations for alloy 9 (Table 1) are illustrated in FIG. 8. This structure results in a maximum hardness at the exterior surface that is preferably 700 to 1300 HV, more preferably 750 to 1250 HV, and most preferably 825 to 1225 HV. The hardness then progressively decreases with increasing distance from the exterior surface (i.e. depth into the part) until it reaches a steady-state value in the core similar to heat treated values discussed herein. Representative examples of the hardness as a function of depth in nitrided case hardened alloys 8 and 9 are seen in **FIG. 9**. As can be seen, the level of nitrogen is increased from the surface down to a depth of at least 200 μm and up to 400 μm. Other alloys listed herein can similarly be case hardened by a nitriding process with similar effectiveness.

Claims:

1. A method of layer-by-layer construction of a metallic part comprising:

supplying particles of an iron-based alloy, the iron-based alloy comprising:

Cr in an amount ranging from 10.0 wt. % to 19.0 wt. %;

Mo in an amount ranging from 0.5 wt. % to 3.0 wt. %;

at least three elements from C, Mn, Cu, Nb, Si and N; and

the balance of said iron-based alloy containing Fe; and

forming an as-built metallic part by powder bed fusing, said powder bed fusing comprising melting the particles into a molten state and cooling and forming one or more solidified layers of the iron-based alloy;

wherein:

one of the at least three elements is Mn, which is present in the iron-based alloy in an amount ranging from greater than 0 to less than or equal to 5.0 wt. %;

when C is in the iron-based alloy, it is present in an amount of 0.35 wt. % or less;

when Cu is in the iron-based alloy, it is present in an amount of 5.0 wt. % or less;

when Nb is in the iron-based alloy, it is present in an amount of 1.0 wt. % or less;

when Si is in the iron-based alloy, it is present in an amount of 1.0 wt. % or less; and

when N is in the iron-based alloy, it is present in an amount of 0.25 wt. % or less;

each of the one or more solidified layers has an as-formed thickness of 2.0 microns to 200.0 microns; and

said as-built metallic part has a tensile strength of at least 1000 MPa, a yield strength of at least 640 MPa, an elongation of at least 3.0%, and a hardness (HV) of at least 375.

2. The method of claim 1, wherein:

Cr is present in said iron-based alloy in an amount ranging from 10.0 wt. % to 18.3 wt. %;

Mo is present in said iron-based alloy in an amount ranging from 0.5 wt. % to 2.5 wt. %;

Mn is present in an amount greater than 0 to 4.0 wt. %

when C is in said iron-based alloy, it is present in an amount of 0.30 wt. % or less;

when Cu is in said iron-based alloy, it is present in an amount of 4.0 wt. % or less;

when Nb is in said iron-based alloy, it is present in an amount of 0.7 wt. % or less;

when Si is in said iron-based alloy, it is present in an amount of 0.7 wt. % or less; and

when N is in said iron-based alloy, it is present in an amount of 0.25 wt.% or less.

3. The method of claim 1, wherein said as-built metallic part has a tensile strength of 1000 MPa to 1900 MPa, a yield strength of 640 MPa to 1500 MPa, an elongation of 3.0% to 25.0%, and a hardness (HV) of 375 to 600.

4. The method of claim 1, wherein each of said one or more layers has a thickness of 5.0 microns to 120.0 microns.

5. The method of claim 1, wherein melting the particles is performed with one or more laser or electron beams with an energy density in the range of 30 J/mm^3 to 500 J/mm^3.

6. The method of claim 1, wherein forming the as-built metallic part is performed in a nitrogen and/or argon atmosphere.

7. The method of claim 1, wherein forming said as-built metallic part comprises forming said one or more solidified layers on a substrate that is preheated to a temperature of less than or equal to 300°C.

8. The method of claim 1, further comprising heating the as-built metallic part at a temperature of greater than 900 °C followed by a gas quench and cooling to form a solutionized metallic part.

9. The method of claim 8, further comprising tempering the solutionized metallic part at a temperature at or above 150 °C to form a tempered metallic part.

10. The method of claim 9, wherein said tempered metallic part has a tensile strength of at least 1000 MPa, a yield strength of at least 900 MPa, an elongation of at least 1.0 % and a hardness (HV) of at least 475.

11. The method of claim 9, wherein the tempered metallic part has a surface, and the method further comprises carburizing the tempered metallic part to increase a level of carbon from the surface down to a depth of 4.0 mm.

12. The method of claim 9, wherein the tempered metallic part has a surface, and the method further comprises nitriding the tempered metallic part to increase a level of nitrogen from the surface down to a depth of 400 μm.

13. The method of claim 1, wherein the iron-based alloy includes at least four elements selected from C, Mn, Cu, Nb, Si and N, wherein one of said at least four elements is Mn.

14. The method of claim 1, wherein said iron-based alloy includes at least five elements selected from C, Mn, Cu, Nb, Si and N, wherein one of said at least five elements is Mn.

15. The method of claim 1, wherein said iron-based alloy includes C, Mn, Cu, Nb, Si and N.

16. The method of claim 1, wherein the iron-based alloy comprises:

Fe in an amount ranging from 82.0 to 86.0 wt. %;

Cr in an amount ranging from 10.5 to 12.0 wt. %;

Mn in an amount ranging from 1.5 to 2.5 wt. %;

Mo in an amount ranging from 0.8 to 1.1 wt. 5;

C in an amount ranging from 0.14 to 0.19 wt. %;

Nb in an amount ranging from 0.02 to 0.06 wt. %;

N in an amount ranging from 0.04 to 0.09 wt. %; and

Si in an amount ranging from 0.25 wt. to 0.75 wt. %

17. The method of claim 1, wherein said iron-based alloy comprises at least 0.14 wt. % Si.

18. The method of claim 1, wherein said iron-based alloy comprises at least 0.1 wt. % C.

19. The method of claim 1, wherein said iron-based alloy comprises at least 0.88 wt. % Ni.

20. The method of claim 1, wherein said iron-based alloy comprises at least 0.12 wt. % Cu.

21. The method of claim 1, wherein said iron-based alloy comprises at least 0.03 wt. % Nb.

22. The method of claim 1, wherein said iron-based alloy comprises at least 0.074 weight % N.

23. The method of claim 1, wherein said iron-based alloy comprises:

at least 0.14 wt. % Si;

at least 0.1 wt. % C; and

at least 0.04 wt. % Nb.

24. The method of claim 1, wherein said iron-based alloy further comprises up to 1.0 wt. % of inevitable impurities.

25. The method of claim 4, wherein the as-built metallic part is crack free.

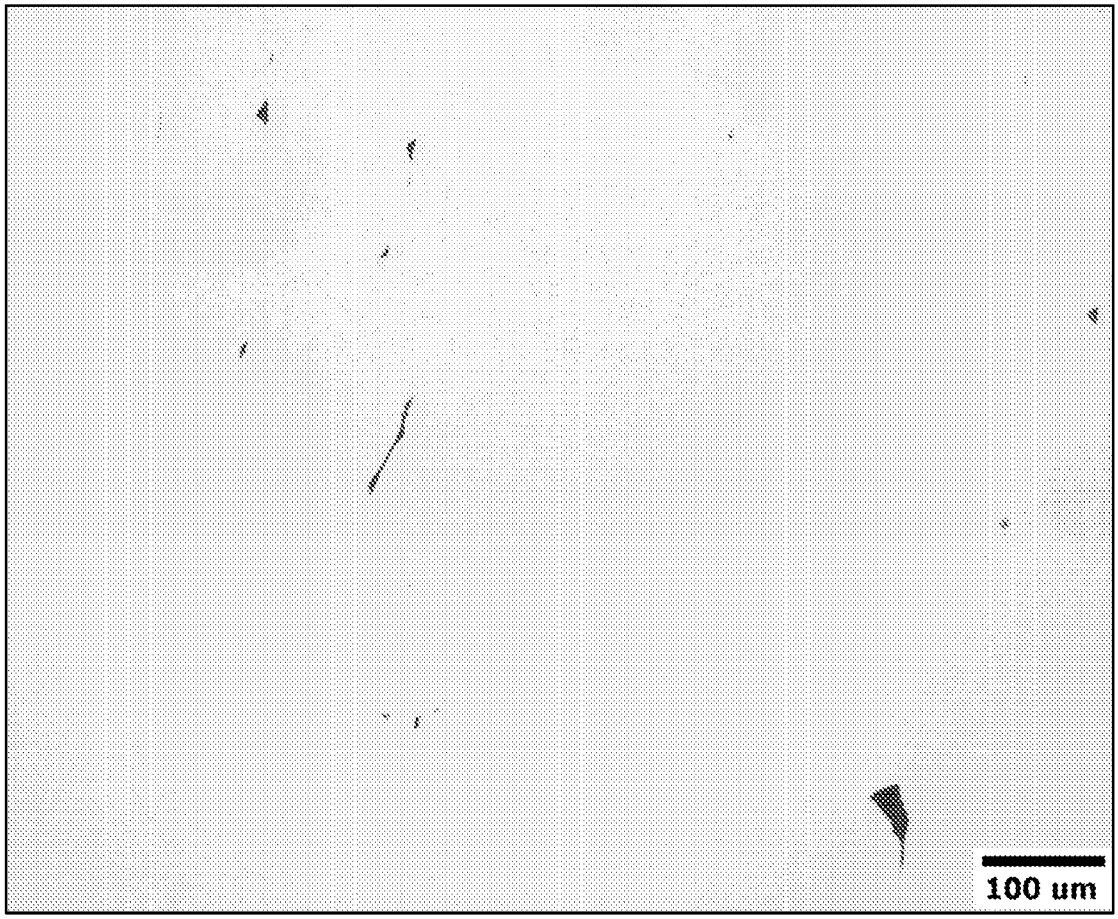


FIG. 1

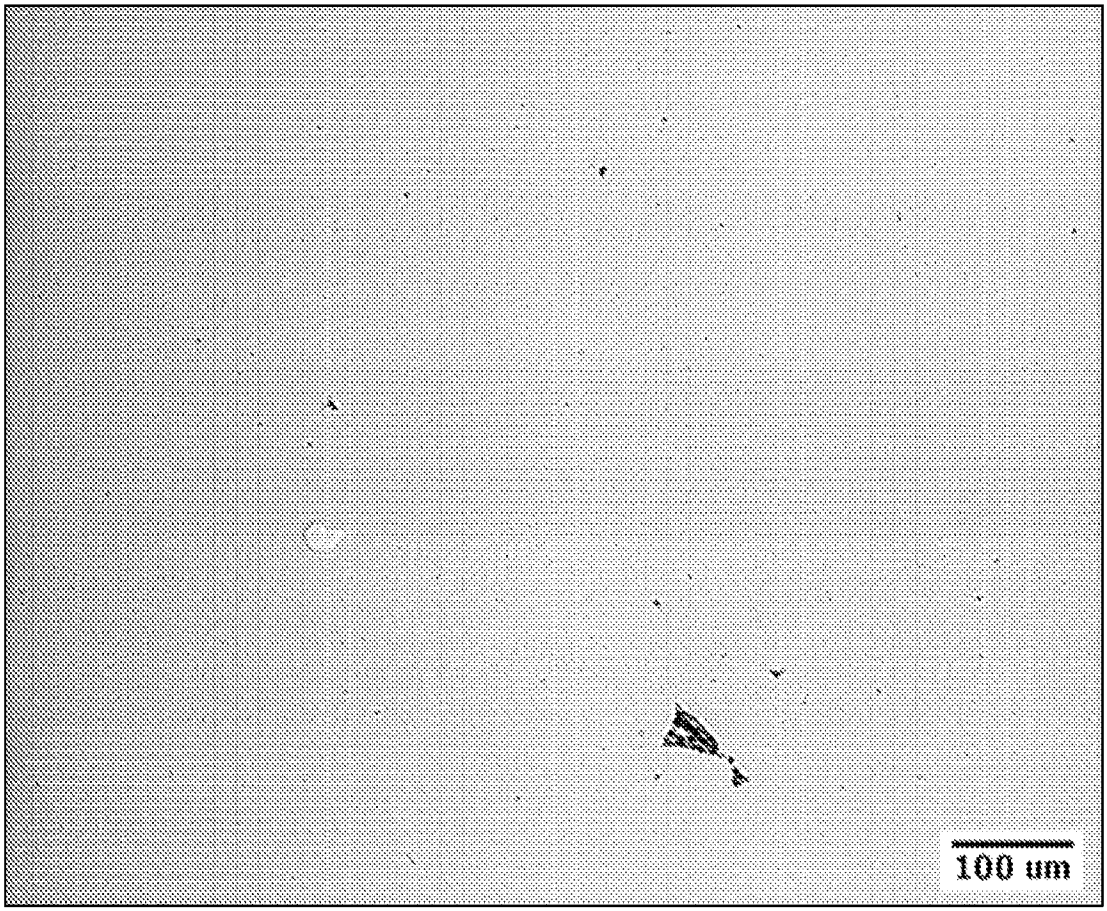


FIG. 2

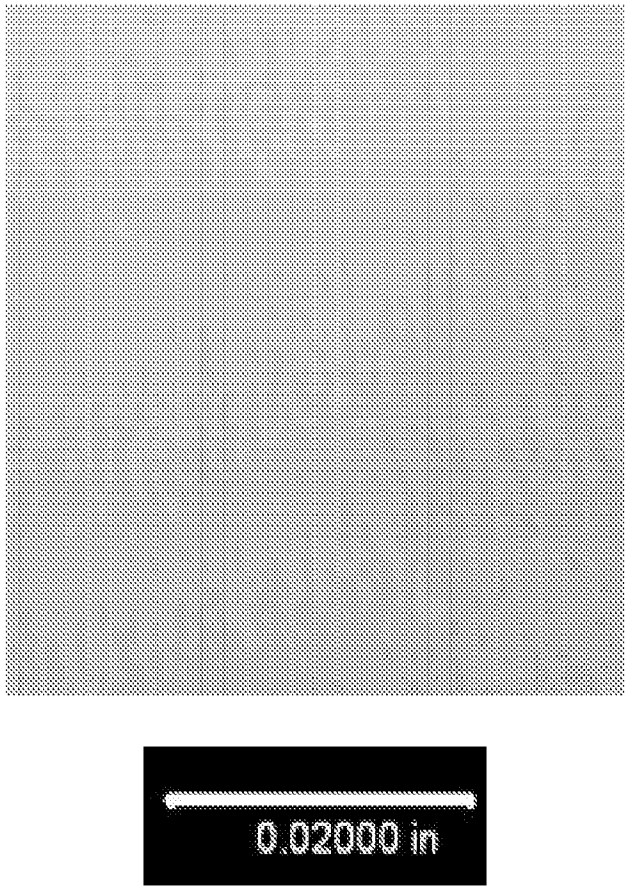


FIG. 3

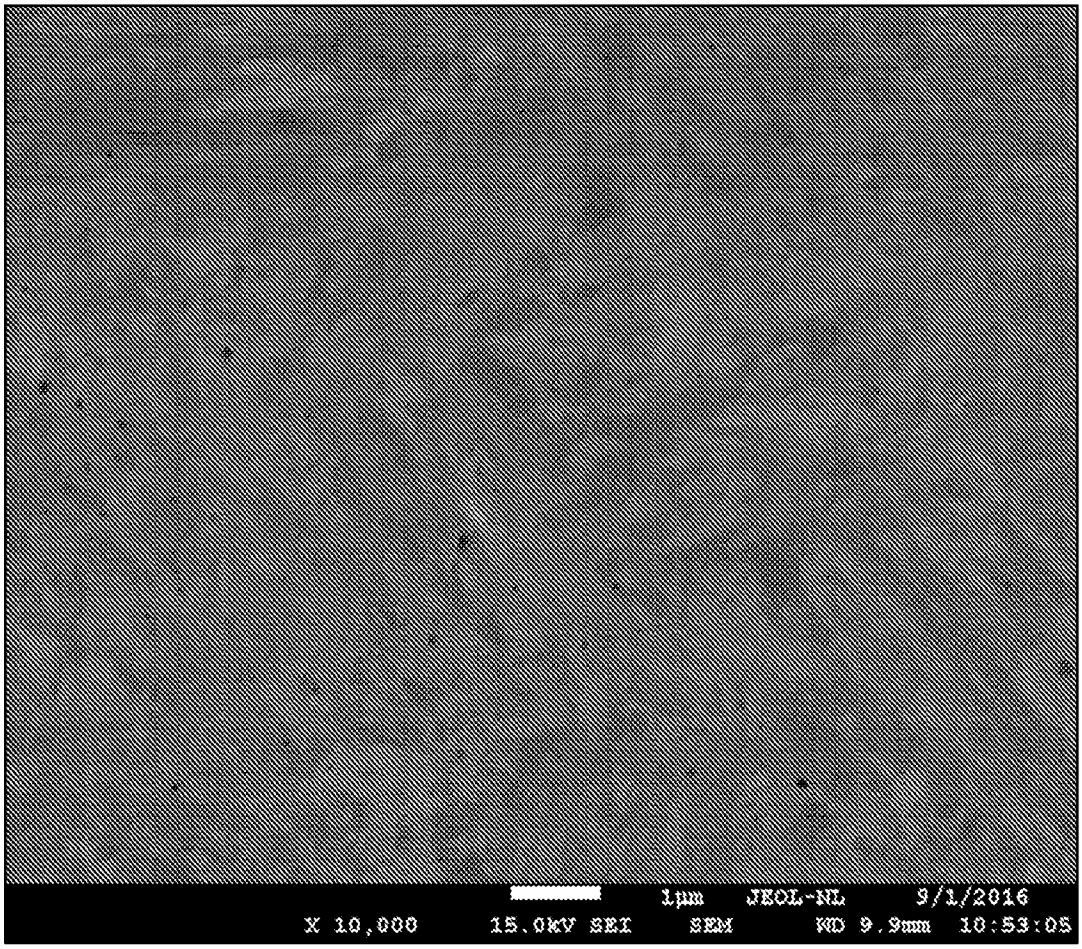


FIG. 4

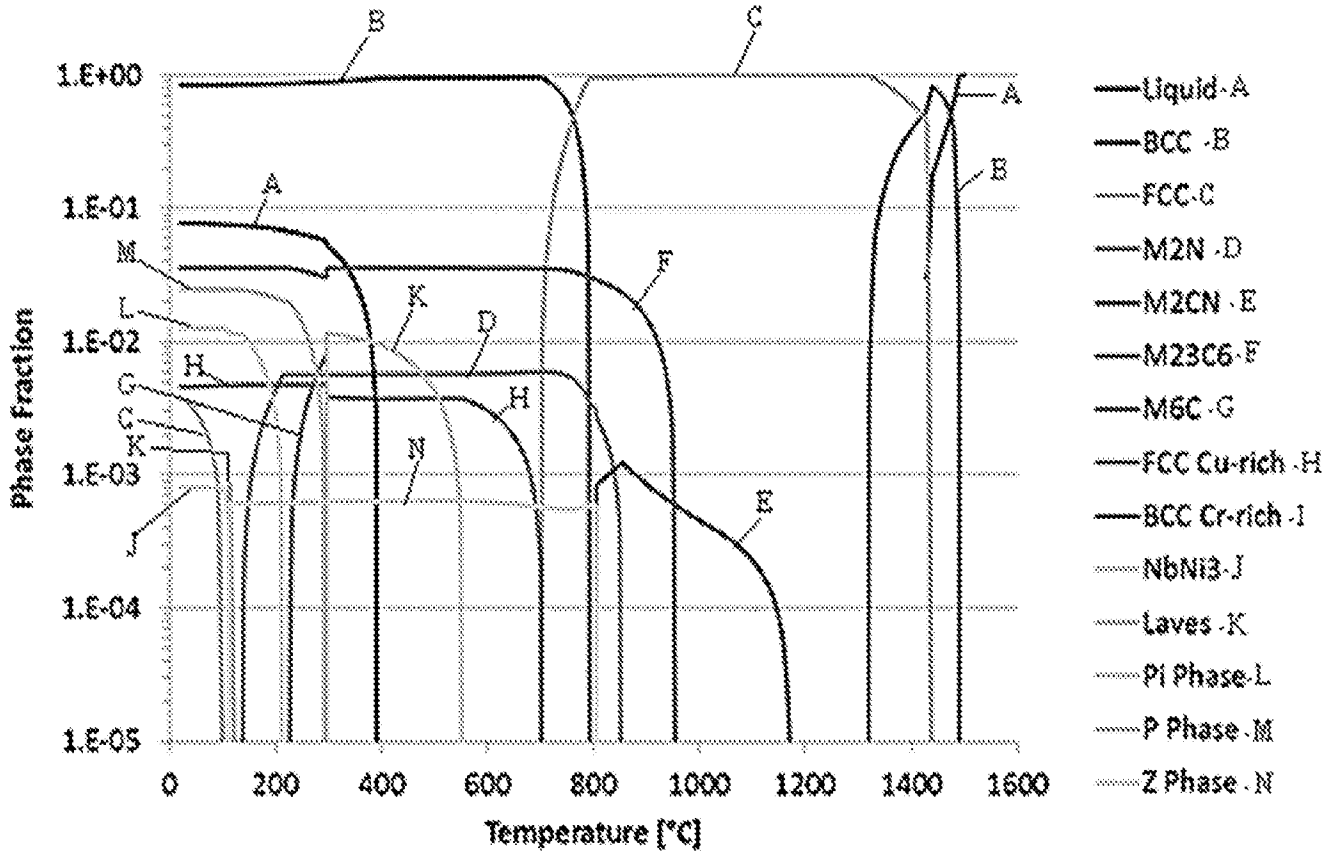

Phase Fraction
1.E+00
1.E-01
1.E-02
1.E-03
1.E-04
1.E-05
0
200
400
600
800
1000
1200
1400
1600
Temperature [°C]
Liquid -A
BCC -B
FCC -C
M2N -D
M2CN -E
M23C6 -F
M6C -G
FCC Cu-rich -H
BCC Cr-rich -I
NbNi3 -J
Laves -K
Pi Phase -L
P Phase -M
Z Phase -N

FIG. 5

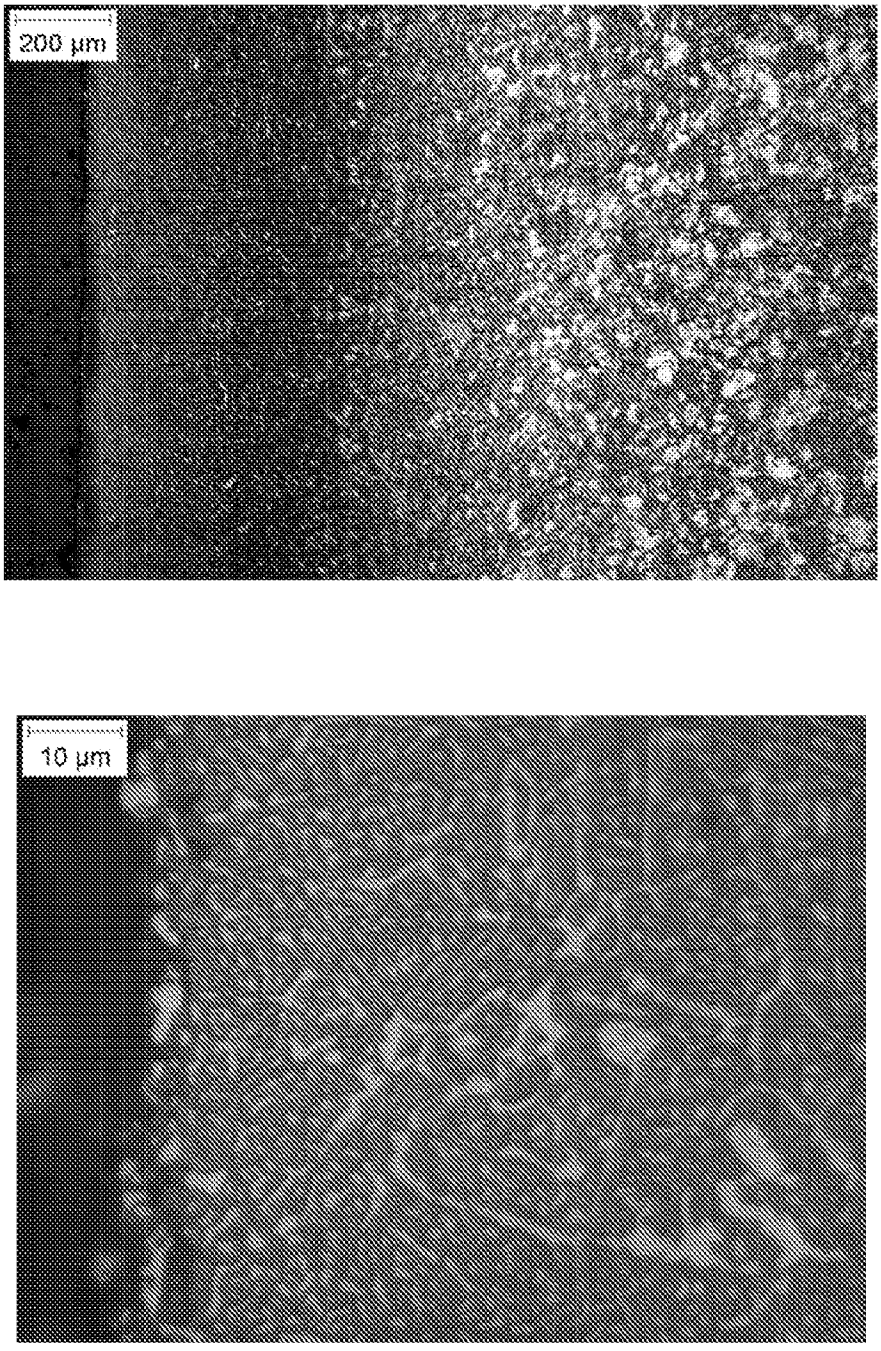


FIG. 6

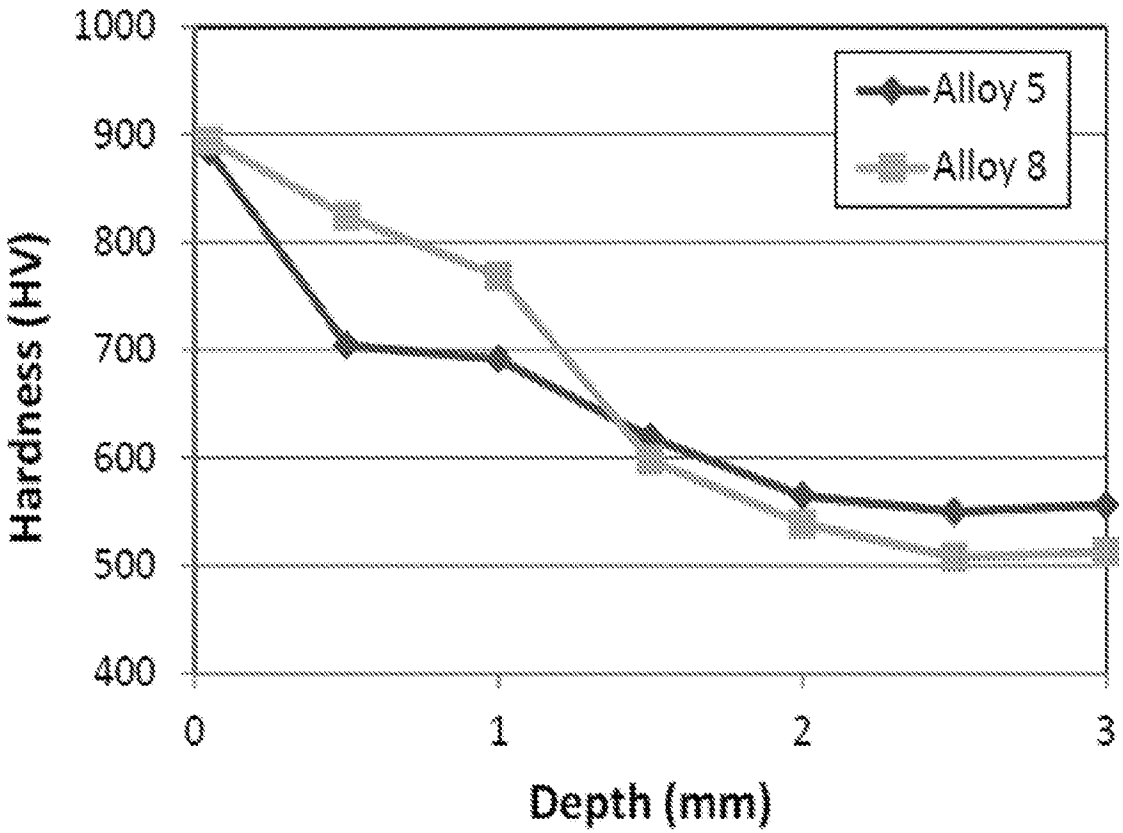

1000
900
800
700
600
500
400
Hardness (HV)
0
1
2
3
Depth (mm)
Alloy 5
Alloy 8

FIG. 7

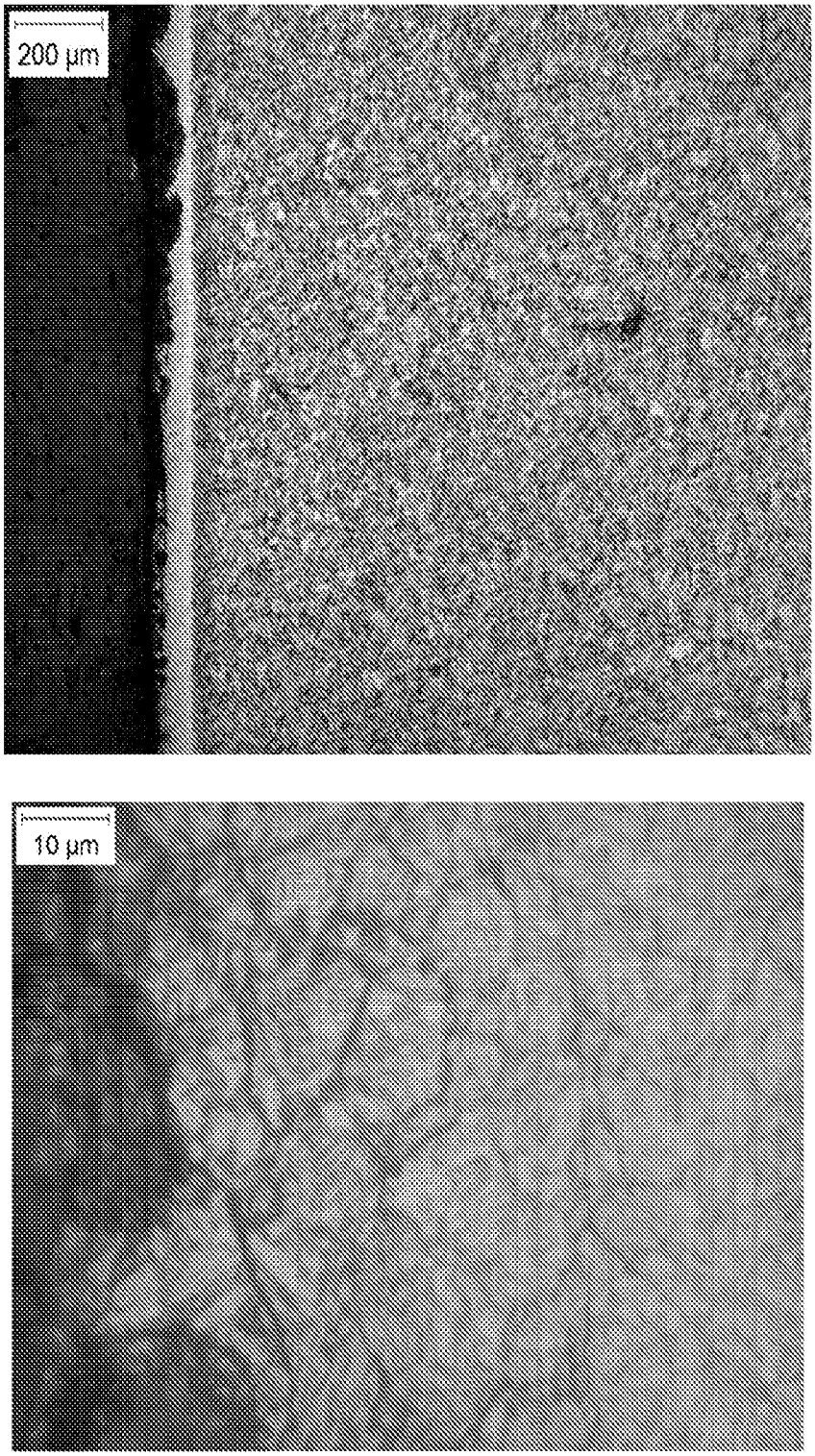


FIG. 8

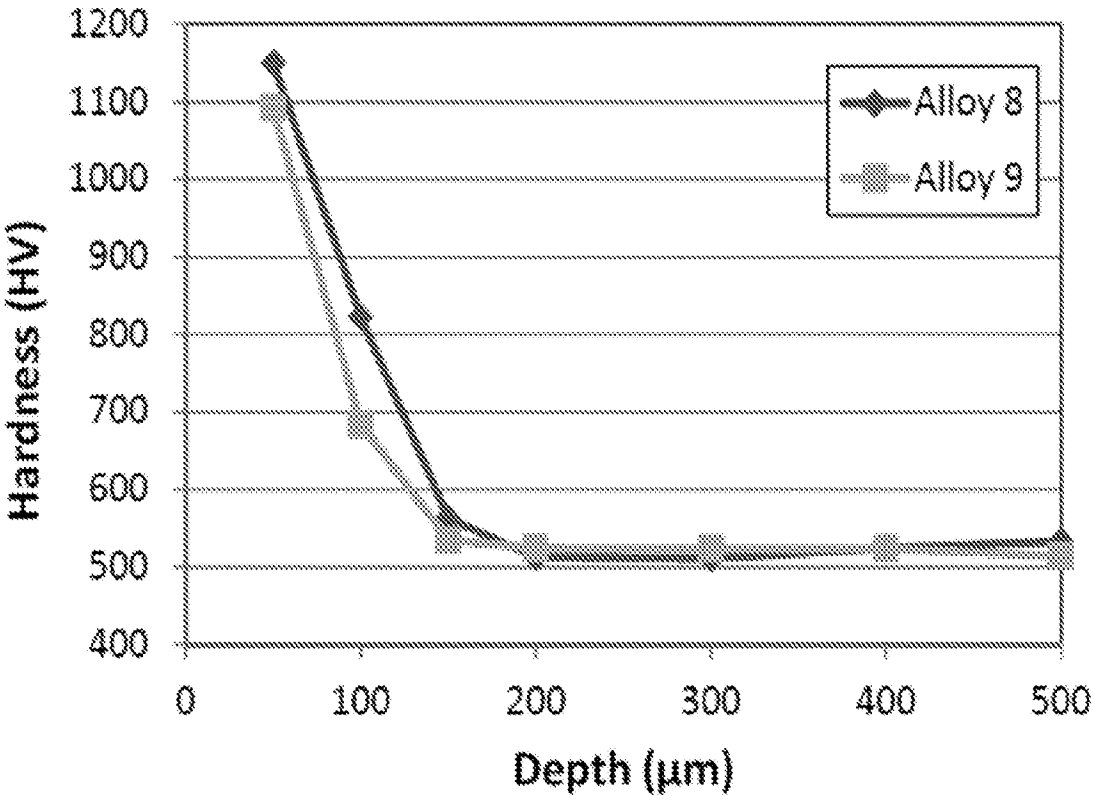

1200
1100
1000
900
800
700
600
500
400
Hardness (HV)
0
100
200
300
400
500
Depth (µm)
Alloy 8
Alloy 9

FIG. 9

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 20/28648

A. CLASSIFICATION OF SUBJECT MATTER

IPC - B23K 26/00; C21D 8/02; C22C 38/00 (2020.01)

CPC - B22F 3/1055; B23K 26/0006; C21D 6/002; C21D 6/004

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)
See Search History document

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

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2018/0119239 A1 (The NanoSteel Company, Inc.) 03 May 2018 (03.05.2018) para [0007], [0009], [0025], [0027], [0029], [0030], [0032], [0053], [0055]-[0058], [0065], [0066], [0068], TABLE 1	1-25
Y	US 2015/0328680 A1 (The NanoSteel Company, Inc.) 19 November 2015 (19.11.2015) Abstract, TABLE 1	1-25
A	US 2018/0010221 A1 (Renishaw PLC) 11 January 2018 (11.01.2018) entire document	1-25
A	US 2018/0214944 A1 (HRL Laboratories, LLC) 02 August 2018 (02.08.2018) entire document	1-25
A	US 2015/0367417 A1 (Velo3D, Inc.) 24 December 2015 (24.12.2015) entire document	1-25

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

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"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
24 June 2020	03 AUG 2020
Name and mailing address of the ISA/US Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-8300	Authorized officer Lee Young Telephone No. PCT Helpdesk: 571-272-4300