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(54) **SELF GENERATED PROTECTIVE
ATMOSPHERE FOR LIQUID METALS**

(52) **U.S. Cl.**
CPC *B22F 9/082* (2013.01); *C22C 37/10*
(2013.01); *B22F 2009/0844* (2013.01)

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(57) **ABSTRACT**

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An improved method of manufacturing a cast part by sand casting, permanent mold casting, investment casting, lost foam casting, die casting, or centrifugal casting, or a powder metal material by water, gas, plasma, ultrasonic, or rotating disk atomization is provided. The method includes adding at least one additive to a melted metal material before or during the casting or atomization process. The at least one additive forms a protective gas atmosphere surrounding the melted metal material which is at least three times greater than the volume of melt to be treated. The protective atmosphere prevents introduction or re-introduction of contaminants, such as sulfur (S) and oxygen (O₂), into the material. The cast parts or atomized particles produced include at least one of the following advantages: less internal pores, less internal oxides, median circularity of at least 0.60, median roundness of at least 0.60 and increased sphericity of microstructural phases and/or constituents.

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Related U.S. Application Data

(60) Provisional application No. 62/409,192, filed on Oct. 17, 2016.

Publication Classification

(51) **Int. Cl.**
B22F 9/08 (2006.01)

FIG. 4

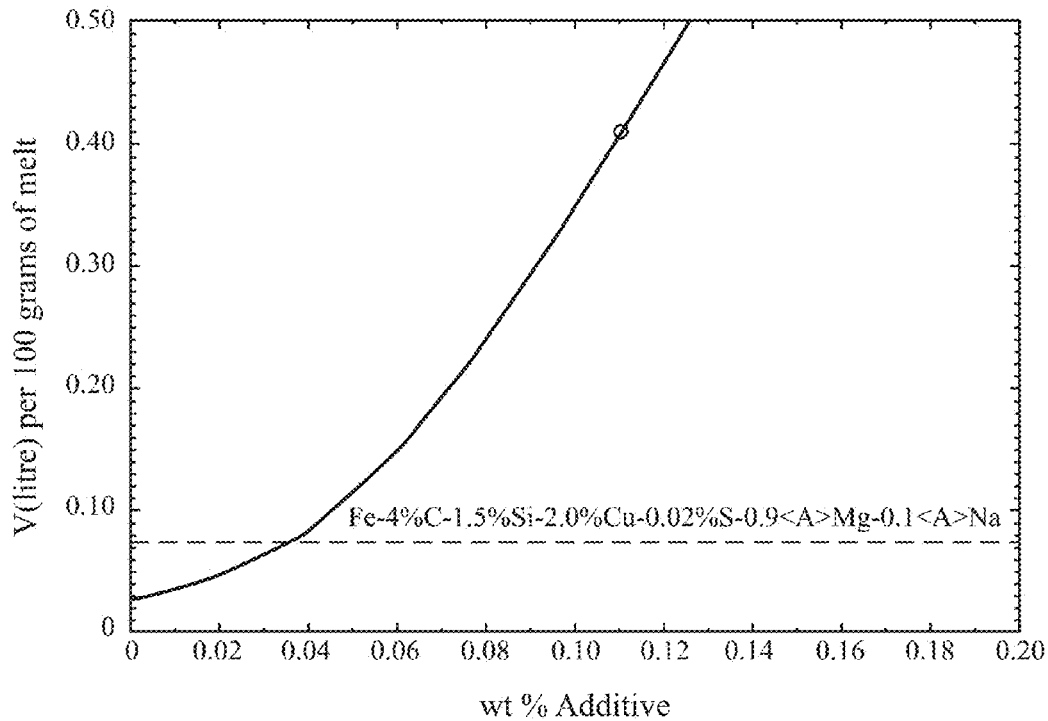


FIG. 5

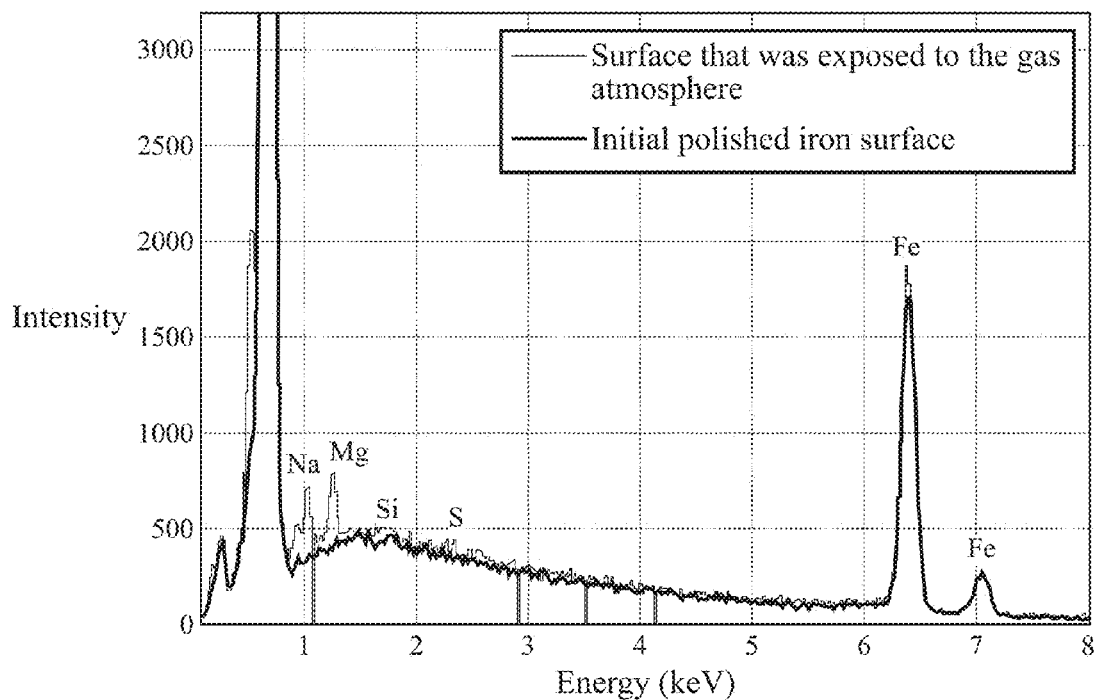


FIG. 6

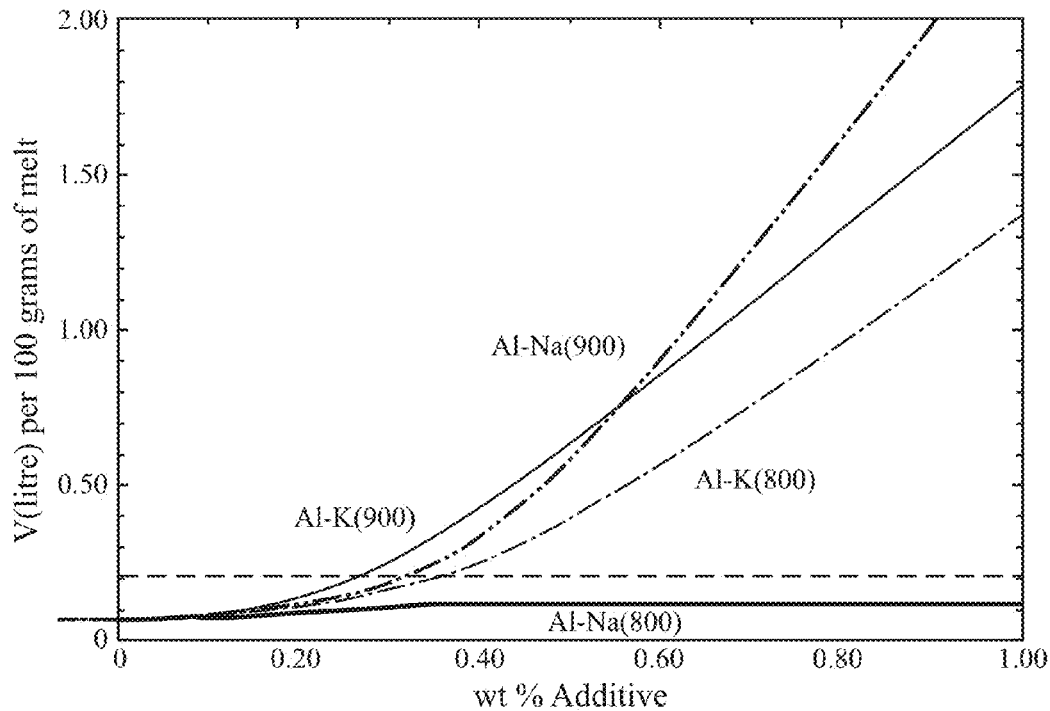


FIG. 7

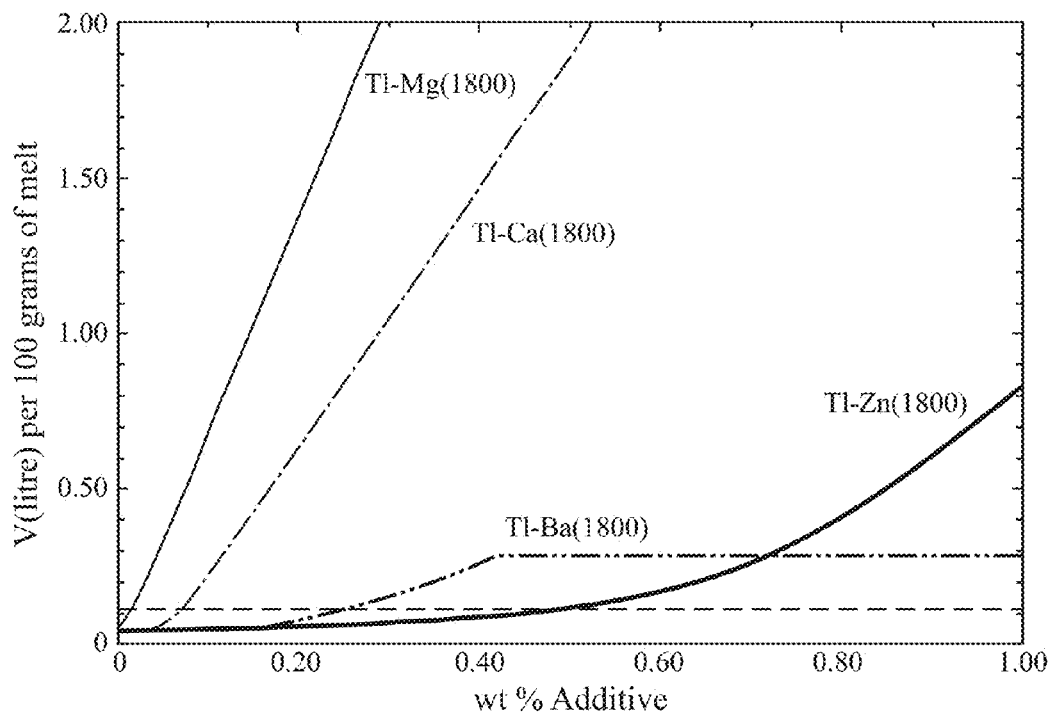


FIG. 8

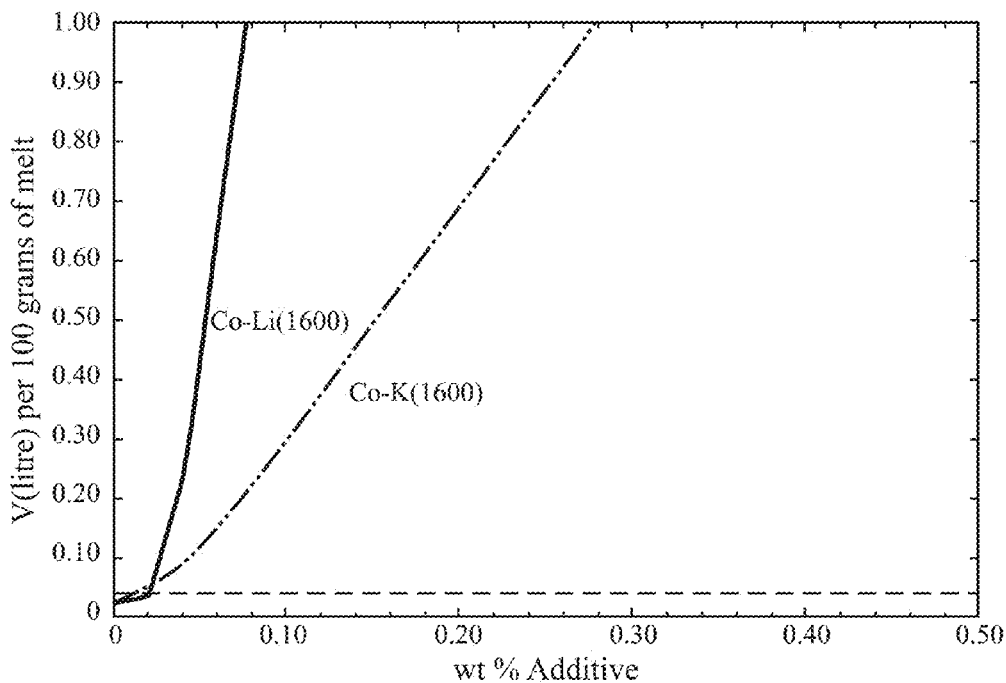


FIG. 9

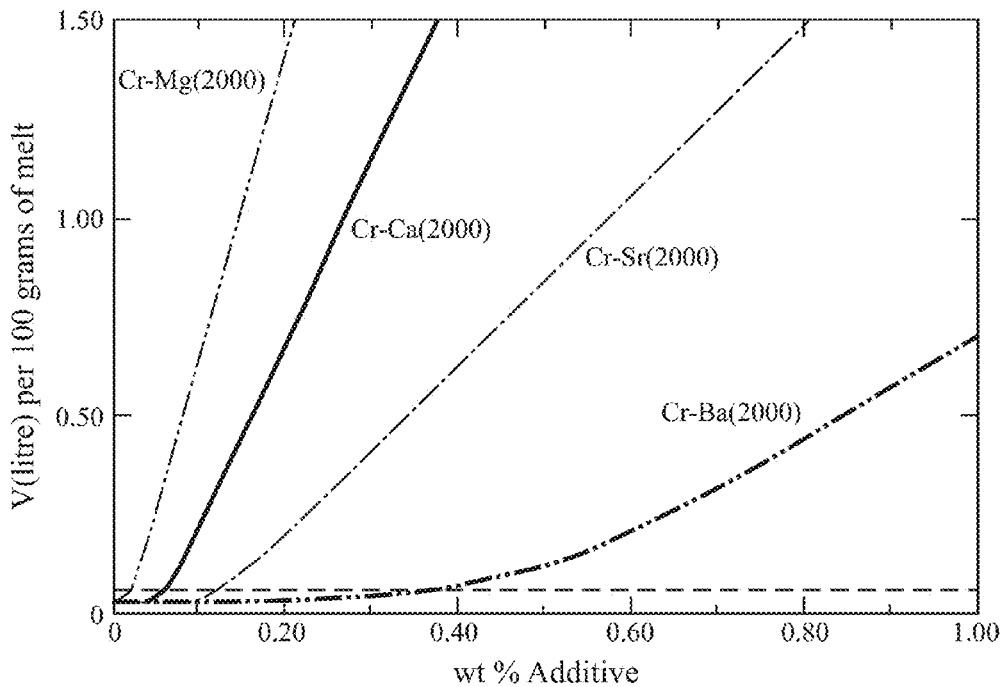


FIG. 10

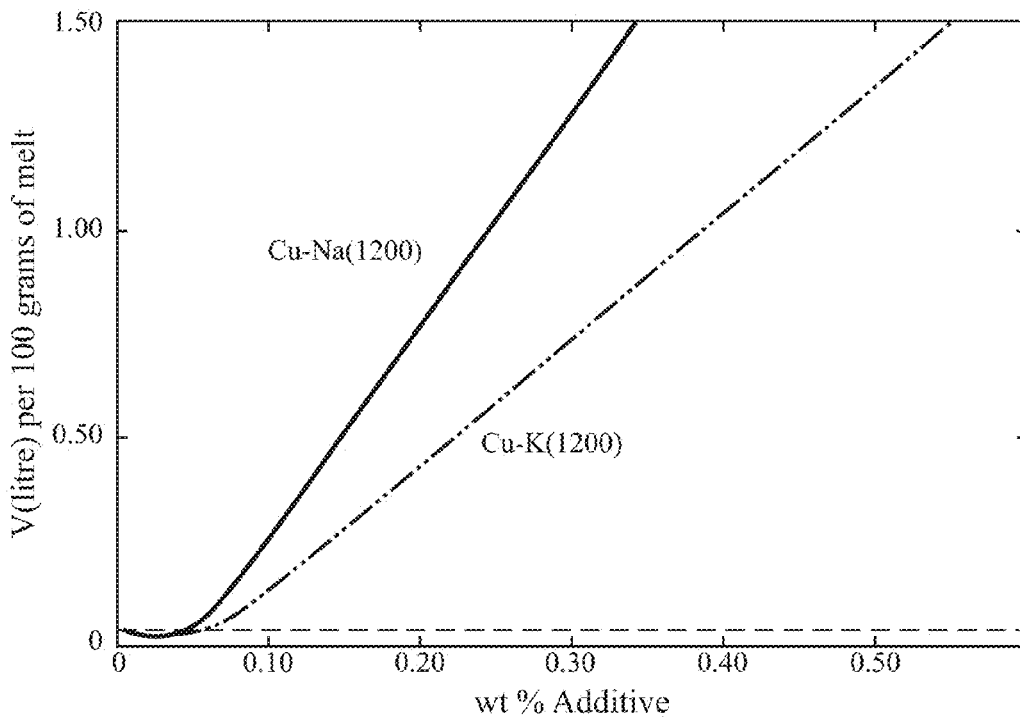


FIG. 11

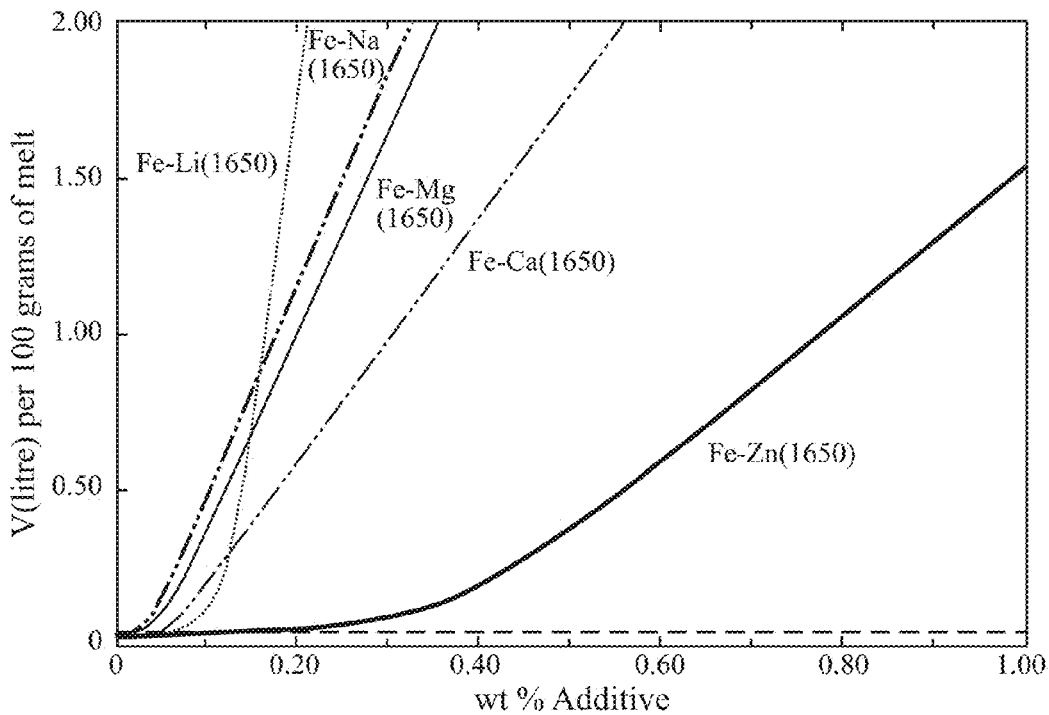


FIG. 12

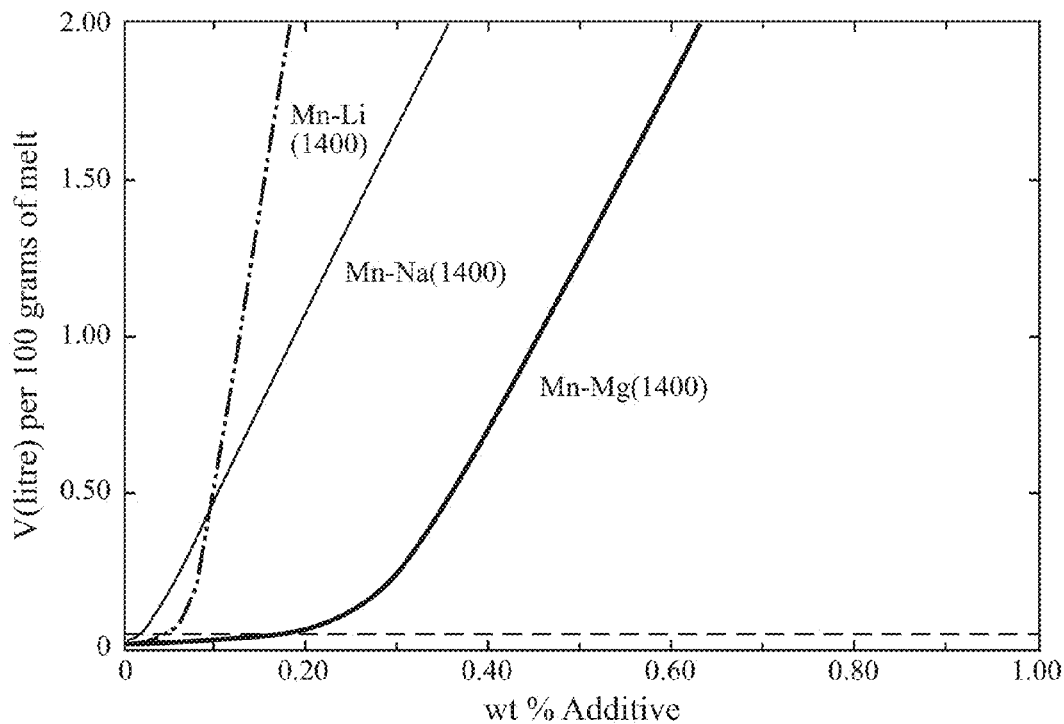


FIG. 13

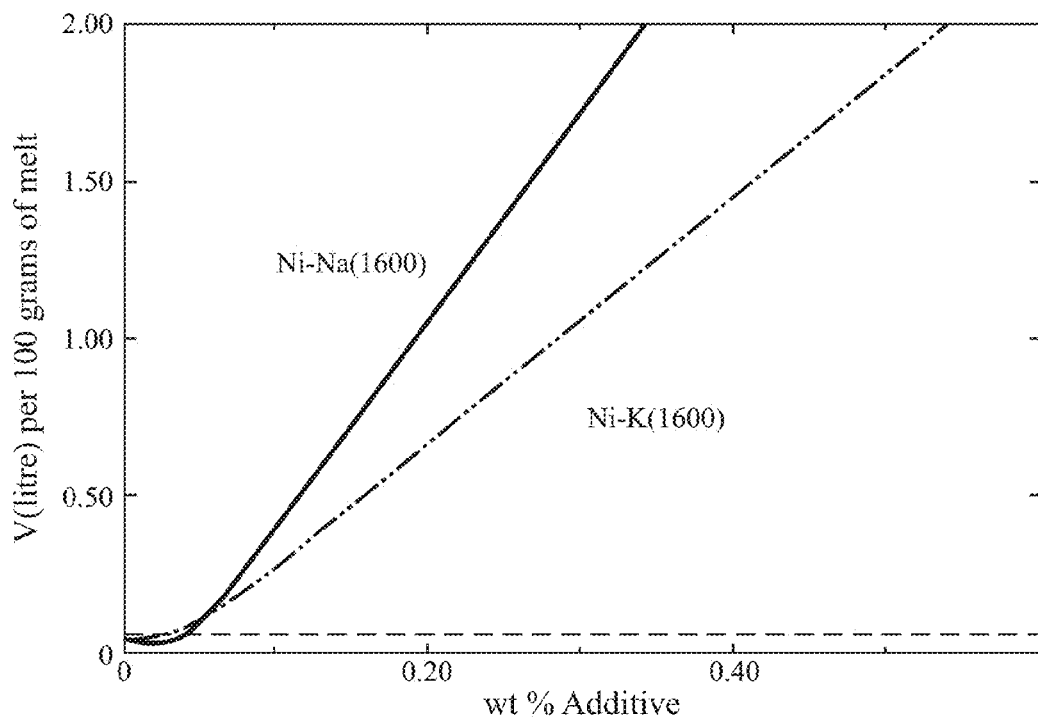


FIG. 14

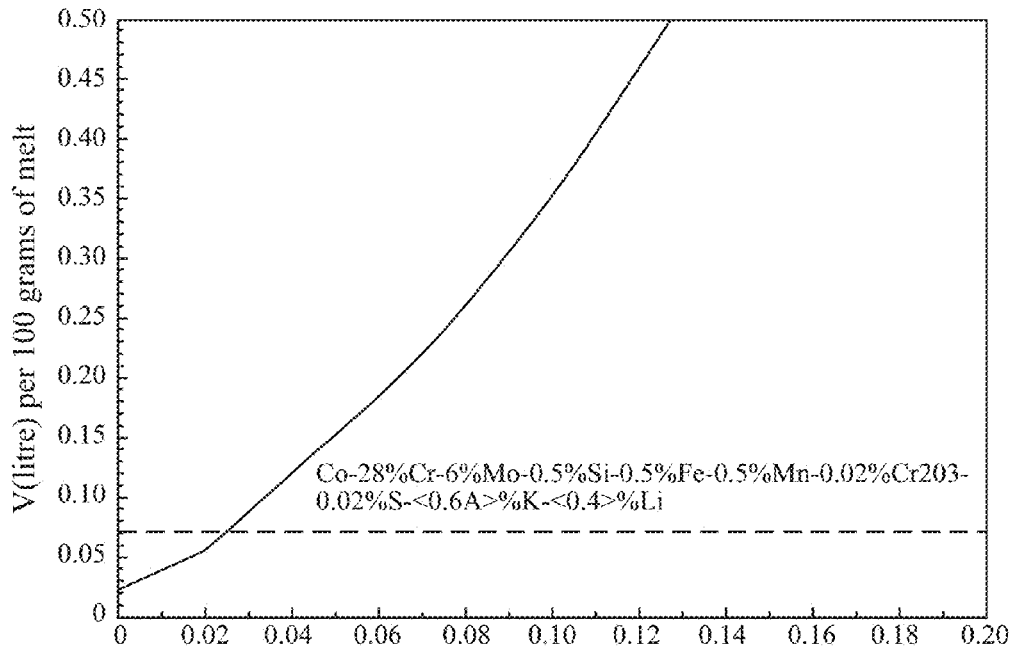


FIG. 15

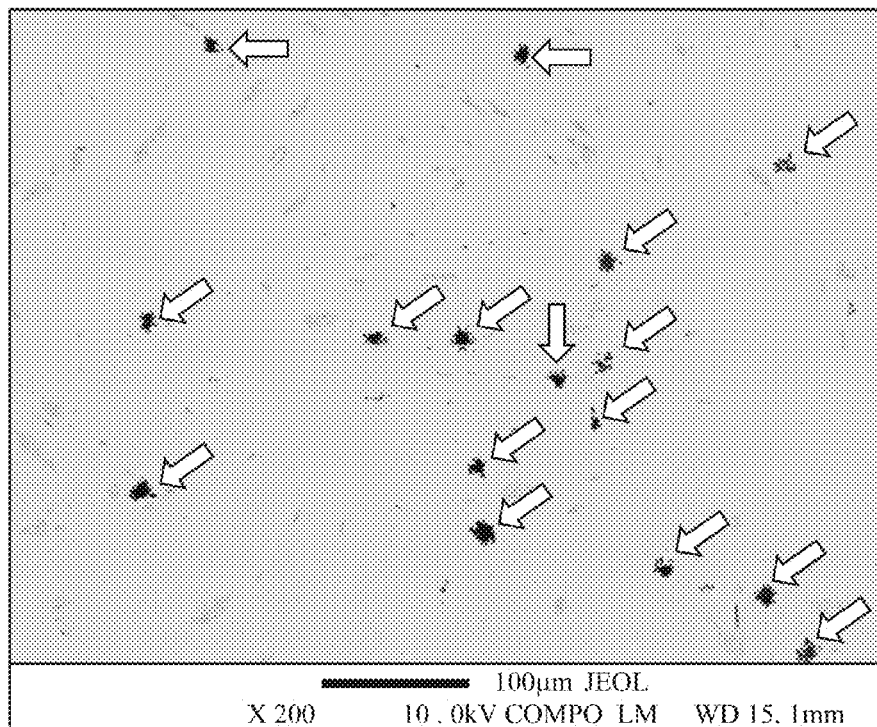


FIG. 16

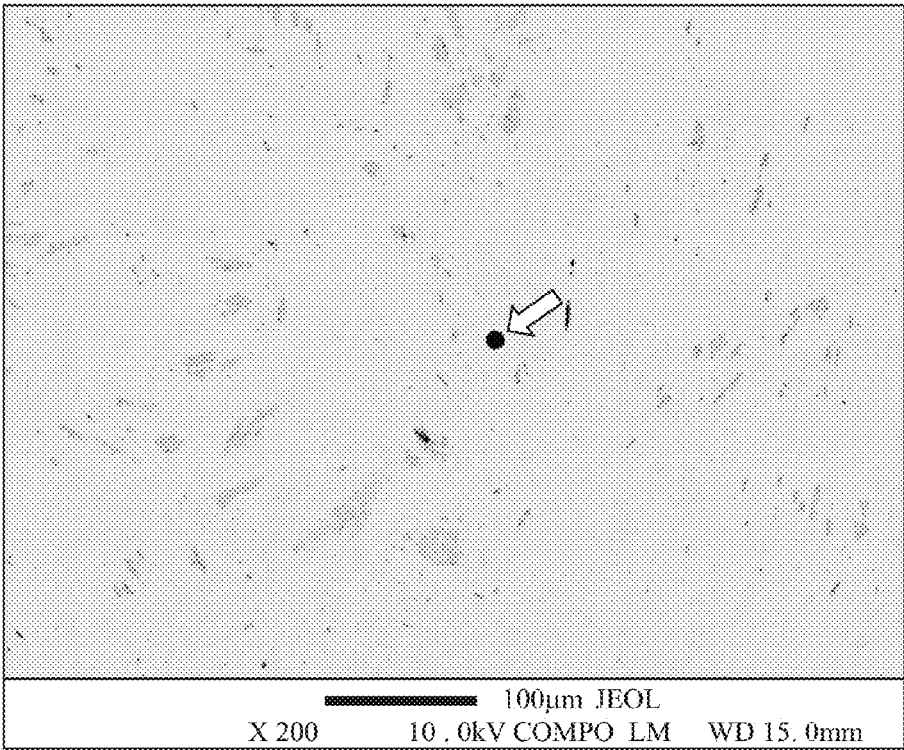


FIG. 17

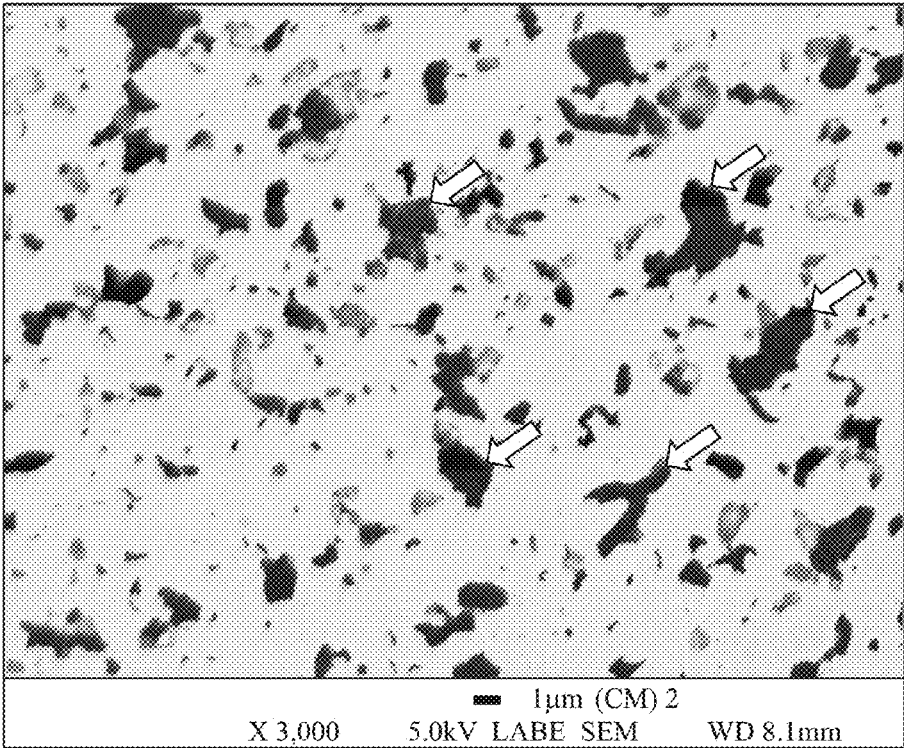


FIG. 18

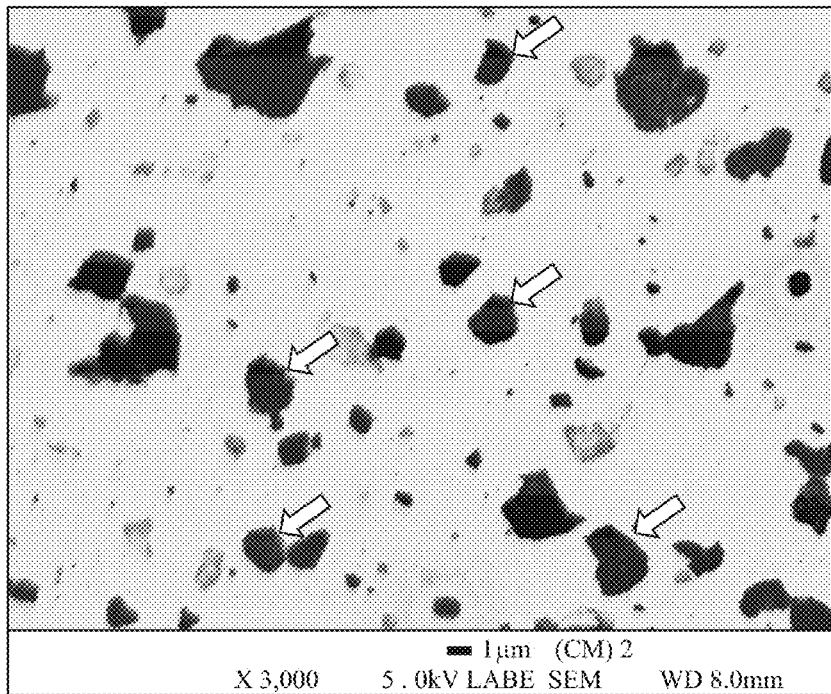


FIG. 19

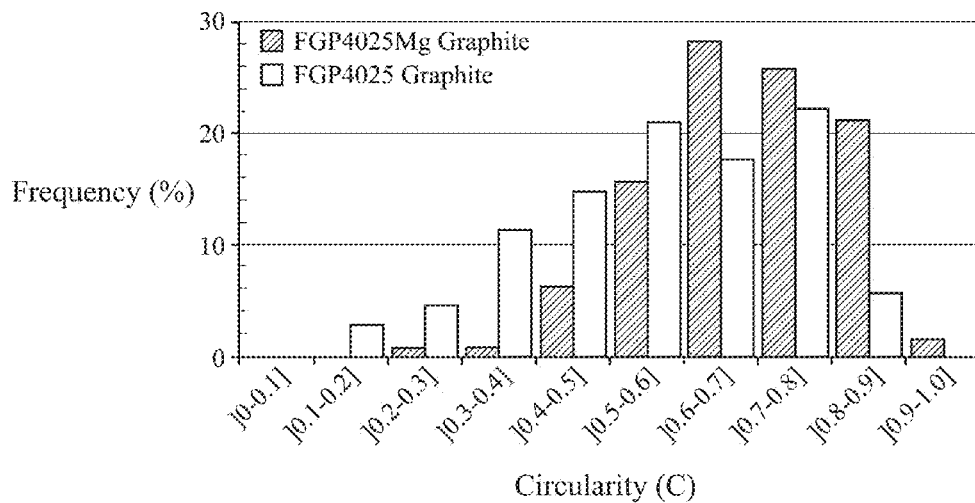


FIG. 20

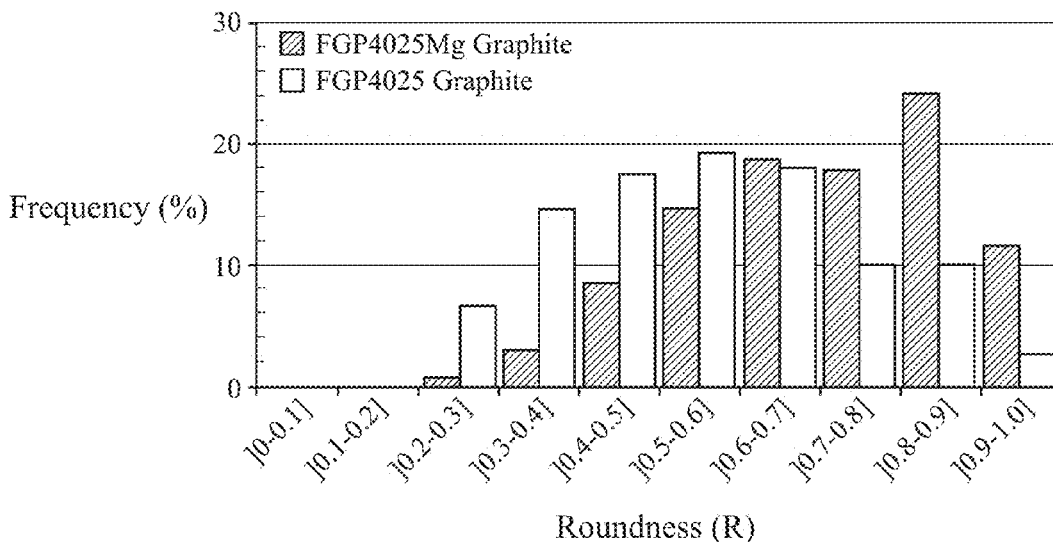


FIG. 21

Circularity (C)		
Graphite Nodules	FGP4025	FGP4025Mg
Number of Nodules Analysed	176	128
Average of the Circularity	0.57	0.69
Standard Deviation	0.17	0.13
Median of the Circularity	0.57	0.70
Absolute % of nodules in [0.6-1.0]	45.5	76.6
Absolute % of nodules in [0.7-1.0]	27.8	48.4
Absolute % of nodules in [0.8-1.0]	5.7	22.7
Absolute % of nodules in [0.9-1.0]	0.0	1.6
Relative %change - Average	n/a	+21
Relative %change - Median		+22
Relative %change - [0.6-1.0]		+68
Relative %change - [0.7-1.0]		+74
Relative %change - [0.8-1.0]		+299
Relative %change - [0.9-1.0]		++

FIG. 22

Roundness (R)		
Graphite Nodules	FGP4025	FGP4025Mg
Number of Nodules Analysed	176	128
Average of the Roundness	0.57	0.71
Standard Deviation	0.18	0.16
Median of the Roundness	0.56	0.73
Absolute % of nodules in [0.6-1.0]	41.5	72.7
Absolute % of nodules in [0.7-1.0]	23.3	53.9
Absolute % of nodules in [0.8-1.0]	13.1	35.9
Absolute % of nodules in [0.9-1.0]	2.8	11.7
Relative %change - Average	n/a	+25
Relative %change - Median		+30
Relative %change - [0.6-1.0]		+75
Relative %change - [0.7-1.0]		+131
Relative %change - [0.8-1.0]		+175
Relative %change - [0.9-1.0]		+313

FIG. 23

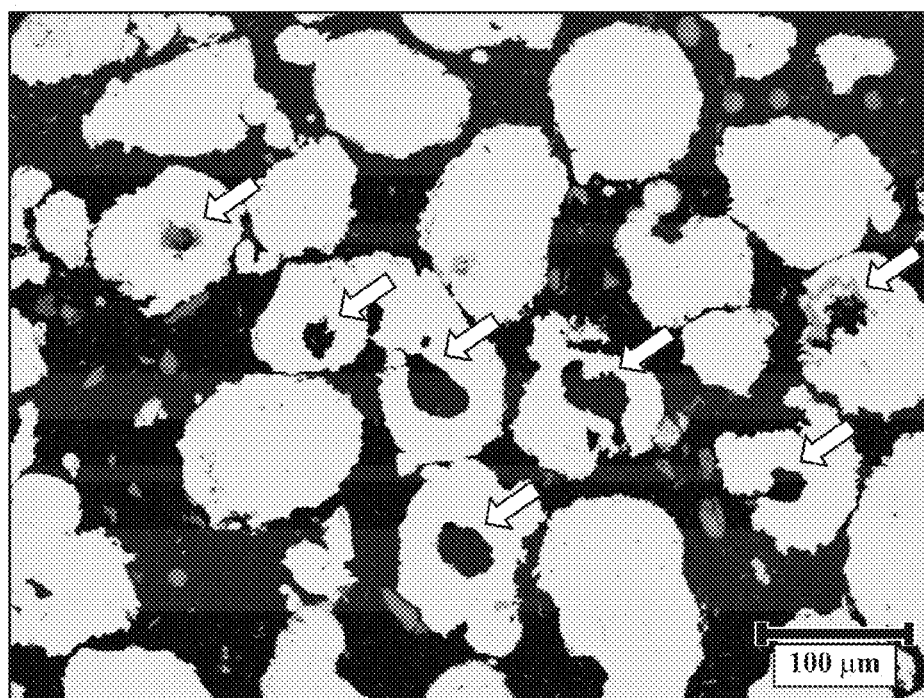


FIG. 24

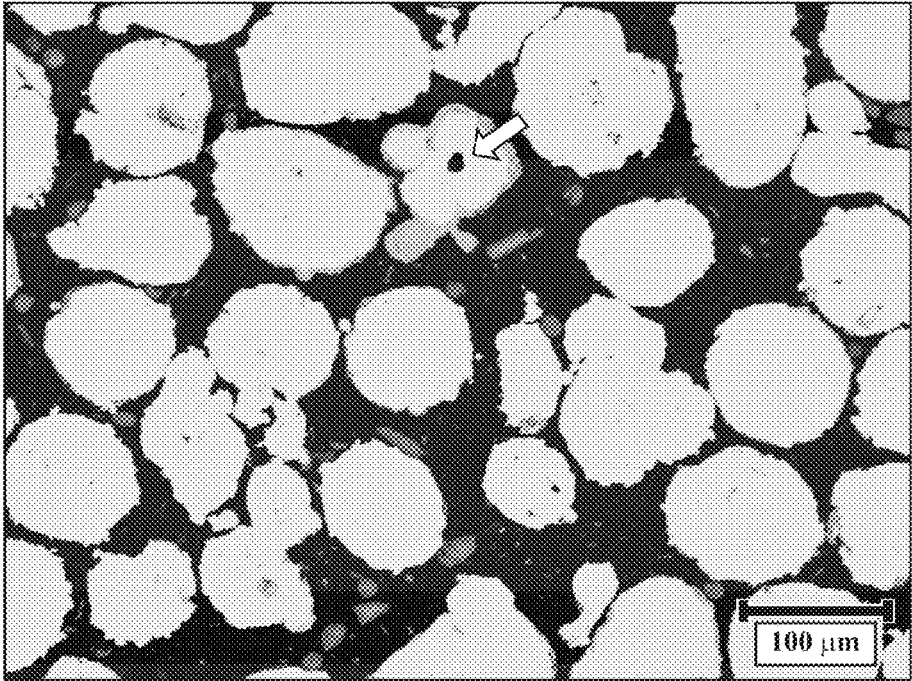
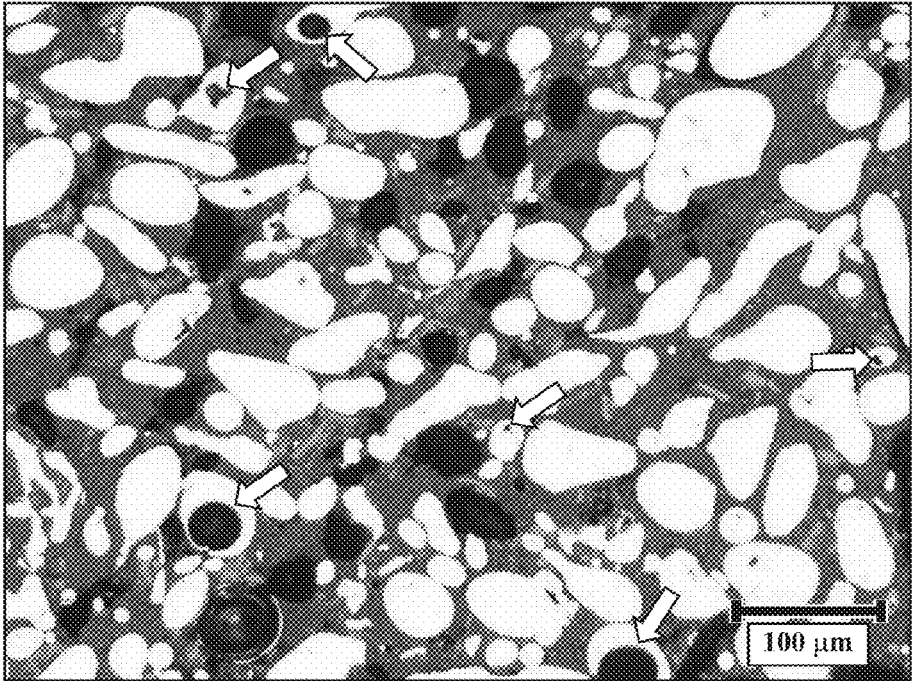


FIG. 25



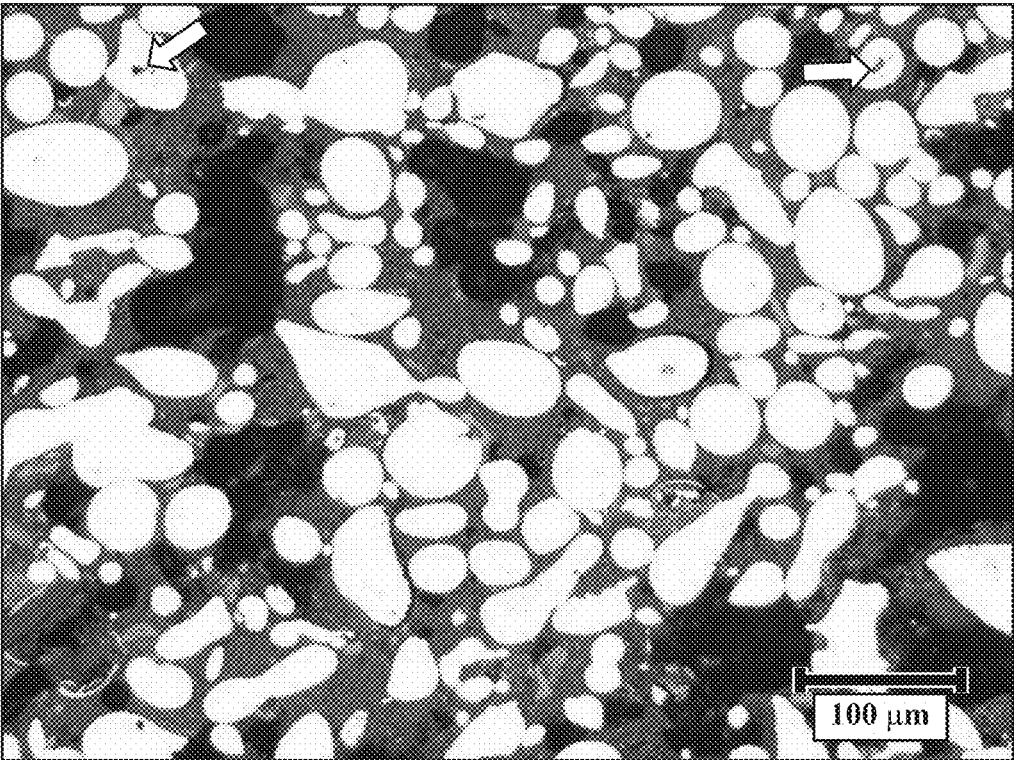


FIG. 26

Materials	C	Si	Mg*	Na**	Cr	Ni	Mn	Mo	Cu	S
High Carbon Steel alloyed with Si	1.40	1.05	0	0	0	0	0.03	0	0	0.012
High Carbon Steel alloyed with Si + Mg	1.34	1.12	0.18	0	0	0	0.04	0	0	0.011
Hypereutectic Cast Iron	4.00	2.25	0	0	0	0	0.02	0	0	0.012
Hypereutectic Cast Iron + Mg	4.08	2.38	0.22	0	0	0	0.03	0	0	0.006
304 Stainless Steel	0.06	0.28	0	0	17.32	9.64	1.24	0.23	0.44	0.026
304 Stainless Steel + Mg	0.06	0.29	0.15	0	17.34	9.46	1.27	0.23	0.45	0.026
Hypereutectic Cast Iron alloyed with Cu + Mg/Na	4.20	1.50	0.10	0.01	0	0	0.02	0	2.0	0.02

*Amount of Mg added to the melt.

** Estimated amount that was added to the melt.

FIG. 27

SELF GENERATED PROTECTIVE ATMOSPHERE FOR LIQUID METALS

CROSS REFERENCE TO RELATED APPLICATION

[0001] This U.S. utility patent application claims priority to U.S. provisional patent application No. 62/409,192, filed Oct. 17, 2016, the contents of which is incorporated herein by reference in its entirety.

BACKGROUND OF THE INVENTION

1. Field of the Invention

[0002] This invention relates generally to metal materials, and more particularly to melted metal materials which are either atomized or solidified to form powder metals or castings, and methods of forming the same.

2. Related Art

[0003] Powder metal materials can be formed by various processes such as by water atomization, gas atomization, plasma atomization, ultrasonic atomization or rotating disk. Powder metal materials are used in various different technologies such as pressed and sintered, metal injection molding, and additive manufacturing. Metal castings are also commonly used in various technologies, including both automotive and non-automotive parts, and produced by various processes such as by sand casting, permanent mold casting, investment casting, lost foam casting, die casting, or centrifugal casting. Both atomization and casting processes begin with a melted metal material. Common atomization processes include applying a fluid (water, gas, oil, ultrasonic, or plasma) to the melted metal material to form a plurality of particles. The casting process typically includes pouring the melted metal material into a mold having a desired shape, and allowing the liquid metal to solidify before removing the metal part from the mold.

SUMMARY

[0004] One aspect of the invention provides a method of manufacturing a powder metal material. This method includes adding at least one additive to a melted base metal material, the at least one additive forming a protective gas atmosphere surrounding the melted base metal material which has a volume of at least three times greater than the volume of the melted base metal material to be treated; and atomizing the melted base metal material after adding at least some of the at least one additive to produce a plurality of particles. Another aspect of the invention provides a powder metal material formed from the melted metal material with the self-generated protective atmosphere.

[0005] Another aspect of the invention provides a method of manufacturing a cast part. The method includes adding at least one additive to a melted base metal material, the at least one additive forming a protective gas atmosphere surrounding the melted base metal material which has a volume of at least three times greater than the volume of the melted base metal material to be treated; and casting the melted metal material after adding at least some of the at least one additive. Another aspect of the invention provides a casting formed from the melted metal material with the self-generated protective atmosphere.

[0006] Both methods include manufacturing a self-generated protective atmosphere in the melted base metal material. Adding the at least one additive to the melted base metal material can improve the quality of the melt. The at least one additive can create the protective atmosphere which acts as a protective barrier against oxidation. The protective atmosphere also acts as a barrier to prevent impurities, such as sulfur (S) and/or oxygen (O₂), from entering or re-entering into the melted metal material. Thus, the at least one additive can limit oxidation during the melting and pouring phases of the process and limit the amount of internal oxides. Additionally, physical structures of powder particles and/or microstructural features in the solidified metal material can be altered to improve or influence the material properties. For example, the at least one additive can also contribute to the microstructural engineering of precipitate, such as size and morphology.

[0007] When the melted metal material is atomized, the at least one additive can engineer the shape and morphology of the resulting powder particles. Also in the case of powder atomization, the at least one additive improves the roundness and sphericity of the resulting powder particles. The amount of internal porosities in powders and castings can also be lowered.

[0008] The atomizing step can also include producing a plurality of particles having a spherical shape. The sphericity of the particles and that of the shape of microstructural phases or constituents in the atomized particles or castings in the as-atomized, as-cast or heat treated state, can be determined by two image analysis indicators, specifically circularity and roundness, according to the following formulas:

$$\text{Circularity } (C) = 4\pi \times (\text{Area}) / (\text{Perimeter})^2$$

$$\text{Roundness } (R) = 4\pi (\text{Area}) / (\pi \times [\text{Major axis}]^2) = 1/AR$$

$$\text{wherein } AR = [\text{Major axis}] / [\text{Minor axis}].$$

[0009] The image analysis indicators can be calculated using open source software, such as ImageJ (<http://imagej.nih.gov/ij/>). A sphericity index value of 1.0 indicates a perfect circle.

BRIEF DESCRIPTION OF THE DRAWINGS

[0010] Other advantages of the present invention will be readily appreciated, as the same becomes better understood by reference to the following detailed description when considered in connection with the accompanying drawings wherein:

[0011] FIGS. 1 to 3 present additives (cells marked with an "x") that will create a protective gas atmosphere, those that will react with oxides, and those that will react with sulfur respectively for various chemical systems (Al, Cu, Mn, Ni, Co, Fe, Ti, and Cr);

[0012] FIG. 4 presents a curve of the calculated total volume of gas that is generated as a function of the amount of additive(s) for an example composition;

[0013] FIG. 5 is a graph showing EDS spectra that were experimentally acquired on a polished pure iron surface before and after it was exposed to the atmosphere on top of the tundish during an atomization process of the powder that is described in FIG. 4;

[0014] FIG. 6 is a graph showing the calculated volume of gas generated by sodium (Na) and potassium (K) additives

in aluminum at different temperatures (800 and 900 Celsius), wherein the dashed line shows the inferior limit of gas;

[0015] FIG. 7 is a graph showing the calculated volume of gas generated by different additives in titanium at a temperature of 1800 Celsius, wherein the dashed line shows the inferior limit of gas;

[0016] FIG. 8 is a graph showing the calculated volume of gas generated by different additives in cobalt at a temperature of 1600 Celsius, wherein the dashed line shows the inferior limit of gas;

[0017] FIG. 9 is a graph showing the calculated volume of gas generated by different additives in chromium at a temperature of 2000 Celsius, wherein the dashed line shows the inferior limit of gas;

[0018] FIG. 10 is a graph showing the calculated volume of gas generated by different additives in copper at a temperature of 1200 Celsius, wherein the dashed line shows the inferior limit of gas;

[0019] FIG. 11 is a graph showing the calculated volume of gas generated by different additives in iron at a temperature of 1650 Celsius, wherein the dashed line shows the inferior limit of gas;

[0020] FIG. 12 is a graph showing the calculated volume of gas generated by different additives in manganese at a temperature of 1400 Celsius, wherein the dashed line shows the inferior limit of gas;

[0021] FIG. 13 is a graph showing the calculated volume of gas generated by different additives in nickel at a temperature of 1600 Celsius, wherein the dashed line shows the inferior limit of gas;

[0022] FIG. 14 is a graph showing the calculated total volume of gas that is obtained per 100 grams of melt of a complex cobalt alloy at a temperature of 1600 Celsius as a function of the amount of additive (K and Li);

[0023] FIG. 15 is a backscattered electron micrograph of a water atomized hypereutectic cast iron powder without added magnesium in which many irregular primary graphite nodules precipitated on internal silicon oxides that were introduced in the melt during the pouring step of the atomization process;

[0024] FIG. 16 is a backscattered electron micrograph of another water atomized hypereutectic cast iron powder with added magnesium in which one spherical primary graphite nodule precipitated on a heterogeneous oxide nuclei that contains Mg during the atomization process;

[0025] FIG. 17 is a backscattered electron micrograph of a water atomized hypereutectic cast iron powder that contains about 4.0% C and 2.3% Si without added magnesium wherein graphite nodules which grew in the solid state during a post heat treatment process are present;

[0026] FIG. 18 is a photomicrograph of another water atomized hypereutectic cast iron powder with added magnesium, according to an example embodiment, wherein more spherical graphite nodules compared to those presented in FIG. 17, which grew in the solid state during a post heat treatment process are present;

[0027] FIG. 19 illustrates the circularity frequency distribution of the graphite nodules that were observed in the water atomized hypereutectic cast iron powders presented in FIGS. 17 and 18;

[0028] FIG. 20 illustrates the roundness frequency distribution of the graphite nodules that were observed in the water atomized hypereutectic cast iron powders presented in FIGS. 17 and 18;

[0029] FIG. 21 is a table illustrating numerical data for the circularity of the graphite nodules that grew in the solid state for two hypereutectic cast iron powders that were observed in FIGS. 17 and 18;

[0030] FIG. 22 is a table illustrating numerical data for the roundness of the graphite nodules that grew in the solid state for two hypereutectic cast iron powders that were observed in FIGS. 17 and 18;

[0031] FIG. 23 is a backscattered electron micrograph of a water atomized stainless steel powder without added magnesium screened at $-80/+200$ mesh (between 177 and 74 microns), wherein the red arrows point to internal porosities;

[0032] FIG. 24 is a backscattered electron micrograph of another water atomized stainless steel powder with added magnesium screened at $-80/+200$ mesh (between 177 and 74 microns), wherein one red arrow points to only one smaller internal porosity compared to those of FIG. 23;

[0033] FIG. 25 is an optical photomicrograph of a water atomized high carbon steel alloyed with silicon powder that contains about 1.3% C and 1.1% Si without added magnesium screened at -200 mesh (74 microns and less) wherein the red arrows point to internal porosities;

[0034] FIG. 26 is an optical photomicrograph of a comparative water atomized high carbon steel alloyed with silicon that contains about 1.4% C and 1.1% Si with added magnesium screened at -200 mesh (74 microns and less) according to one example embodiment wherein the red arrows point to fewer internal porosities than the powder of FIG. 25; and

[0035] FIG. 27 includes a table listing compositions evaluated.

DETAILED DESCRIPTION OF EXEMPLARY EMBODIMENTS

[0036] One aspect of the invention includes an improved method of manufacturing a powder metal material by water or gas atomization or any other atomization process that requires that the material to be atomized goes through the creation of a bath of liquid metal such as plasma atomization, ultrasonic atomization or rotating disk atomization, by adding at least one additive to a melted metal material before and/or during the atomization process. Another aspect of the invention includes an improved method of manufacturing a casting by processes such as sand casting, permanent mold casting, investment casting, lost foam casting, die casting, or centrifugal casting from a melted metal material by adding at least one additive to the melted metal material. The at least one additive forms a protective gas atmosphere surrounding the melted metal material which is at least three times greater than the volume of melt to be treated.

[0037] The protective atmosphere created by the at least one additive that is added to the melted material acts as a barrier to prevent impurities, such as sulfur (S) and/or oxygen (O₂) or others, from entering or re-entering into the melted metal material by pushing them away from the surface of the melted material as the protective gas is coming out of the melt. The additive(s) that forms the protective gas atmosphere can also react with the dissolved sulfur in the melt and/or the oxides that were in suspension in the melt before the introduction of the additive(s). Reaction of the additive(s) with the dissolved sulfur in the melt will increase the sphericity of atomized particles formed from the melt

and/or increase that of the microstructural phases and constituents in the atomized particles or castings.

[0038] When water atomization is employed, adding the additive(s) to the melted metal material can increase the sphericity of the atomized particles to a level approaching the sphericity of particles formed by gas atomization, but with reduced costs compared to gas atomization. Adding the additive(s) to the melted metal material can also produce cleaner particles by limiting the formation and the entrainment of new oxides from the surface of the melt and by reacting with those already present in the melt before the introduction of the additive(s). These oxides can form as bifilms where films of oxides are folded on themselves leaving a weak interface in between the oxide films. The additive(s) can also lower the amount and size of internal porosity, a problem encountered in atomized powders. The additive(s) can also increase the sphericity of microstructural constituents and/or phases formed in the atomized particles and/or during a subsequent heat treatment process. For example, if the atomized particles are formed from a cast iron material, at least 50% of the graphite precipitates formed during the post heat treatment process will have a circularity of at least 0.6 and a roundness of at least 0.6.

[0039] When casting is employed, adding the additive(s) to the melted metal material can increase the sphericity of microstructural constituents and/or phases formed in the castings and/or during a subsequent heat treatment process. Adding the additive(s) to the melted metal material can also produce cleaner castings by limiting the formation and the entrainment of new oxides from the surface of the melt and by reacting with those already present in the melt before the introduction of the additive(s). These oxides can form as bifilms where films of oxides are folded on themselves leaving a weak interface in between the oxide films. The additive(s) can also lower the amount and size of internal porosity, a problem encountered in many castings.

[0040] According to one example embodiment, the method begins by melting a base metal material. Many different metal compositions can be used as the base metal material. However, in order to produce enough gas that will act as a protective atmosphere and thus obtain either the desired spherical-shape of the powders and/or more spherical microstructural constituents and/or cleaner particles and/or having less internal pores, the additive(s) must have a low solubility in the metal material. The base material and the additive(s) should be selected such that when the additive(s) are introduced, the volume of protective gas atmosphere generated is at least three times the volume of melted metal material to be treated. For example, if 0.22 weight percent (wt. %) magnesium is added to an iron-rich melt, the generated volume of gas will be about 20 times the inferior limit of gas required to provide a protective atmosphere which is defined as three times the initial volume of melt to be treated.

[0041] The base metal material typically includes at least one of aluminum (Al), copper (Cu), manganese (Mn), nickel (Ni), cobalt (Co), iron (Fe), titanium (Ti), and chromium (Cr). The base metal material can comprise pure Al, Cu, Mn, Ni, Co, Fe, Ti, or Cr. Aluminum-rich, copper-rich, manganese-rich, nickel-rich, cobalt-rich, iron-rich, titanium-rich and chromium-rich alloys, or an alloy including at least 50 wt. % of Al, Cu, Mn, Ni, Co, Fe, Ti, and/or Cr are also well suited for use as the starting base metal material. Mixtures of these base metal materials in different proportions are also

well suited for use as the starting material such as, but not limited to, Al—Cu, Fe—Ni, Fe—Co, Fe—Ni—Co, Ni—Cr, Ti—Cu, and Co—Cr alloys. The alloys can also include at least one of the following as alloying elements, as long as they will stay in solution in the melt of the alloy of interest: silver (Ag), boron (B), barium (Ba), beryllium (Be), carbon (C), calcium (Ca), cerium (Ce), gallium (Ga), germanium (Ge), potassium (K), lanthanum (La), lithium (Li), magnesium (Mg), molybdenum (Mo), nitrogen (N), sodium (Na), niobium (Nb), phosphorus (P), sulfur (S), scandium (Sc), silicon (Si), tin (Sn), strontium (Sr), tantalum (Ta), vanadium (V), tungsten (W), yttrium (Y), zinc (Zn), and zirconium (Zr).

[0042] There is a distinction to be made between the elements described as “alloying elements” and those described as “additives.” Alloying elements will stay in solution in the base metal material and/or form different phases/constituents in the final parts/powders.

[0043] Alloying elements will impact the microstructure and the properties of the parts. For instance, C in Fe will form cementite, which increases strength. Additives are defined as elements added to the melt to either create a protective gas atmosphere, react with S and/or with oxides. FIGS. 1 to 3 include a complete list of additives in different base metal materials. One particular element can be an alloying element in one base material but be an additive in a different base material. For instance, Mg is an alloying element in Al-rich alloys but is an additive in Fe-rich alloys. According to one example embodiment, to create a gaseous protective atmosphere in an Al-Mg alloy, K and/or Na should be used as an additive and the melt temperature should be selected according to the selected additive(s). For example, since Mg is used as an alloying element in aluminum alloys (the Al-5000 series) it will not generate a protective gas atmosphere.

[0044] However, the starting metal material is not limited to the above mentioned compositions. Other metal compositions can be used, as long as the additive has a low solubility in the selected material and generates a sufficient amount of protective gas atmosphere. Some additives that are used to create the gaseous protective atmosphere will naturally react with the dissolved sulfur in the melt to create more stable compounds and thus increase the surface tension. This is the case for Mg in Fe-rich systems in which solid MgS will precipitate. However, some additives will create a protective atmosphere but will not react with the dissolved sulfur, as is the case with Na in Fe-rich systems. In these situations, a combination of different additives must be used to increase surface tension and create a protective atmosphere.

[0045] As mentioned above, various different additives could be added to the melted metal material to achieve the increased protective atmosphere and the other advantages mentioned above. The additive(s) selected depends on the composition of the base metal material. For example the at least one additive can include at least one of K, Na, Zn, Mg, Li, Ca, Sr, and Ba. The protective gas atmosphere generated by the additive(s) prevents impurities from entering or re-entering into the melted metal material.

[0046] The additives listed above generate different amounts of protective gas atmosphere, depending on the chemical system in which they are used. Some additives are more suited for some systems than others. For example, in aluminum alloys, K and Na are oftentimes preferred. In

copper alloys, K and Na are oftentimes preferred. In manganese alloys, K, Na, Zn, Mg, and Li are oftentimes preferred. In nickel alloys, K and Na are oftentimes preferred. In cobalt alloys, K, Na, Li, and Ca are oftentimes preferred. In iron alloys, K, Na, Zn, Mg, Li, Sr, and Ca are oftentimes preferred. In titanium alloys, Zn, Mg, Li, Ca, and Ba are oftentimes preferred. In chromium alloys, K, Na, Zn, Mg, Li, Sr, Ca, and Ba are oftentimes preferred. Examples are provided in FIG. 1, wherein the preferred additives are marked.

[0047] According to one specific example embodiment, the metal base material is iron-rich and includes Mg which generates the protective gas and also reacts with the sulfur impurity. Alternatively, the base metal material is pure iron and the additive is Mg. According to another specific example, the metal base material is iron-rich and the additives include a mixture of K and Ba. The potassium (K) will generate the protective gas atmosphere, and the barium (Ba) will react with the sulfur.

[0048] The protective atmosphere limits the amount of oxides in the atomized particles and castings and will also limit the size and amount of internal porosities in the atomized particles and castings. Some additives that are used to create the gaseous protective atmosphere will naturally react with oxides that are in suspension in the melt to create more stable compounds and will also change their morphology during the chemical reaction process, for example a Mg additive in Fe-rich systems that contain Si as an alloying element. In these materials, oxides of SiO_2 that could be in the form of bifilms (overlapping films of oxides that are poorly bounded) are in suspension in the melt. One of the reasons explaining that a smaller amount of porosities is observed is that Mg helps to bound the interfaces between the overlapping films, a result of a chemical reaction between Mg and the oxides, creating a stronger interface that cannot be subsequently separated to form pores. The self-generated Mg gaseous atmosphere will limit further oxidation of the surface of the melt, which will limit the amount of internal oxides in the particles. However, some additives will create a protective atmosphere but will not react with the oxides in suspension in the melt, as is the case of Zn in Ti-rich systems. In these situations, a combination of different additives must be used to limit the amount and size of internal porosities. For example, at least one additive could be added to generate the protective gas atmosphere that will prevent impurities from entering or re-entering into the melted metal material, and at least one additive could be added to react with the oxides already in the melt but would not necessarily create a protective gas atmosphere. An example of such a combination of additives in a Ti-rich alloy to create more spherical particle and/or phases and constituents having less internal porosities could be a mixture of Zn to create a protective atmosphere and Sr to react with S and with TiO_2 but without participating in the generation of the protective atmosphere.

[0049] In other words, some additives are more effective in some systems than in others, depending on the type of oxides that are formed. As indicated above, if less internal porosities with smaller sizes are desired, the additive(s) must react with the oxides in suspension in the melt. These oxides are also considered impurities in the melted base metal material, for example, Al_2O_3 in an aluminum-based material, or Fe_2O_3 in an iron-based material. When the melted base metal material is an aluminum alloy or aluminum-

based, the preferred additives to react with the oxides include K, Na, Mg, Li, and Ca. When the melted base metal material is an iron alloy or iron-based, the preferred additives to react with the oxides include K, Na, Zn, Mg, Li, Sr, Ca, and Ba. When the melted base metal material is a titanium alloy or titanium-based, the preferred additives to react with the oxides include Sr, Ca, and Ba. When the melted base metal material is a chromium alloy or chromium-based, the preferred additives to react with the oxides include K, Na, Zn, Mg, Li, Sr, Ca, and Ba. When the melted base metal material is a cobalt alloy or cobalt-based, the preferred additives to react with the oxides include K, Na, Zn, Mg, Li, Sr, Ca, and Ba. When the melted base metal material is a copper alloy or copper-based, the preferred additives to react with the oxides include K, Na, Zn, Mg, Li, Sr, Ca, and Ba. When the melted base metal material is a manganese alloy or manganese-based, the preferred additives to react with the oxides include K, Na, Zn, Mg, Li, Sr, Ca, and Ba. When the melted base metal material is a nickel alloy or nickel-based, the preferred additives to react with the oxides include K, Na, Zn, Mg, Li, Sr, Ca, and Ba. Examples are provided in FIG. 2.

[0050] When the melted base material is iron-based and includes sulfur as an impurity, Zn, Mg, Li, Sr, Ca, and Ba are preferred to react with the sulfur. An example of such a combination of additives in an iron-based material or Fe-rich alloy to create more spherical particle and/or phases and constituents could be a mixture of Na and Ba. Na will create a protective atmosphere and Ba will react with S. When the melted base metal material is a titanium alloy or titanium-based and includes sulfur as an impurity, K, Na, Zn, Mg, Li, Sr, Ca, and Ba are preferred to react with the sulfur. When the melted base metal material is a cobalt alloy or cobalt-based and includes sulfur as an impurity, Na, Mg, Li, Sr, Ca, and Ba are preferred to react with the sulfur. When the melted base metal material is a chromium alloy or chromium based and includes sulfur as an impurity, K, Na, Zn, Mg, Sr, Ca, and Ba are preferred to react with the sulfur. When the melted base metal material is an aluminum alloy or aluminum-based and includes sulfur as an impurity, K, Na, Mg, Li, Sr, Ca, and Ba are preferred to react with the sulfur. When the melted base metal material is a nickel alloy or nickel-based and includes sulfur as an impurity, Mg, Li, Sr, Ca, and Ba are preferred to react with the sulfur. When the melted base metal material is a copper alloy or copper-based and includes sulfur as an impurity, K, Na, Mg, Li, Sr, Ca, and Ba are preferred to react with the sulfur. When the melted base metal material is a manganese alloy or manganese-based and includes sulfur as an impurity, K, Na, Mg, Li, Sr, Ca, and Ba are preferred to react with the sulfur. Examples are provided in FIG. 3.

[0051] In addition, certain additives will successfully generate the protective gas atmosphere, and also react with the sulfur and oxides present as impurities in the melted base metal material. For example, when the melted base metal material is an iron-alloy or iron-based, additives that will generate the protective gas atmosphere and react with the sulfur and oxide impurities include Zn, Mg, Li, Sr, and Ca. When the melted base metal material is a titanium alloy or titanium-based, additives that will generate the protective gas atmosphere and react with the sulfur and oxide impurities include Ca and Ba. When the melted base metal material is a chromium alloy or chromium-based, additives that will generate the protective gas atmosphere and react

with the sulfur and oxide impurities include K, Na, Zn, Mg, Sr, Ca, and Ba. When the melted base metal material is a cobalt alloy or cobalt-based, additives that will generate the protective gas atmosphere and react with the sulfur and oxide impurities include Na, Li, and Ca. When the melted base metal material is an aluminum alloy or aluminum-based, additives that will generate the protective gas atmosphere and react with the sulfur and oxide impurities include K and Na. When the melted base metal material is a copper alloy or copper-based, additives that will generate the protective gas atmosphere and react with the sulfur and oxide impurities include K and Na. When the melted base metal material is a manganese alloy or manganese-based, additives that will generate the protective gas atmosphere and react with the sulfur and oxide impurities include K, Na, Mg, and Li.

[0052] As stated above, the melted metal material can be atomized, for example by water or gas atomization, to form powder metal. Alternatively, the melted metal material can be formed into a casting.

[0053] As alluded to above, the starting base metal material selected oftentimes includes iron in an amount of at least 50.0 wt. %, based on the total weight of the metal material before adding the additive(s). For example, cast irons, highly alloyed cast irons, stainless steels, unalloyed and alloyed steels, tool steels, Maraging steels, or Hadfield steels could be used. According to one example embodiment, the metal material is a steel powder including 1.3 wt. % carbon and 1.1 wt. % silicon. According to another example embodiment, the metal material is a cast iron powder including 4.0 wt. % carbon and 2.3 wt. % silicon. According to another example embodiment, the metal material is a stainless steel powder including 1.2% Mn, 0.30% Si, 0.44% Cu, 0.23% Mo, 17.3% Cr, 9.5% Ni, and other trace elements. As stated above, aluminum alloys (for instance the alloys designated as 2024, 3003, 3004, 6061, 7075, 7475, 5080 and 5082), copper alloys (such as aluminum bronzes, silicon bronzes, and brass), manganese alloys, nickel alloys (for instance the alloy designated as 625), cobalt alloys (such as tribaloy and Haynes188), cobalt-chromium alloys (such as CoCrMo alloys and stellite), titanium alloys (for instance the alloys designated as Ti-6Al-4V or as Ti-6Al), chromium alloys (such as the Kh65NVFT alloy) and any hybrid alloys made from these chemical systems can also be used as the starting powder metal material (for instance, alloys designated as Invar, Monel, Chromel, Alnico, and Nitinol60). These examples are not exhaustive and other metal compositions can be used, as long as the at least one additive (potassium (K), sodium (Na), zinc (Zn), magnesium (Mg), lithium (Li), strontium (Sr), calcium (Ca), and barium (Ba)) has low solubility in the selected material, such that a protective gas atmosphere is formed on top of the melted material to form a total amount of at least three times the initial volume of melt to be treated. FIGS. 4-14 represent the results of calculations and experiments conducted which show the increased volume of protective gas atmosphere generated when the additive(s) are added to the melted metal material according to example embodiments of the invention. FIG. 4 presents a curve of the total volume of gas that is obtained as a function of the amount of additive(s) for an example composition. The additive (here, the additive was a mixture of 90 wt.% Mg and 10 wt.% Na). The alloy is a cast iron powder material (Fe-rich) that contains 4.0% C, 1.5% Si, 0.02% S and 2.0% Cu. This curve was calculated using

the chemical composition of one powder that was water atomized, the amount of additive used in this experiment was 0.11 wt. %, which resulted in about 0.40 liter of protective gas (Mg and Na) for each 100 grams of melt. The dashed line represents the inferior limit of gas that should be obtained to provide a protective atmosphere which is a volume that is three times the initial volume of melt to be treated. In this specific example, the calculated amount of gas is about five times the inferior limit.

[0054] FIG. 5 presents Energy-dispersive X-ray spectroscopy (EDS) spectra that were acquired on a polished pure iron surface before and after it was exposed to the gaseous atmosphere on top of the tundish during the atomization process of the powder that is described in FIG. 4. This confirms that the additives (in this case Mg and Na) formed a gaseous protective atmosphere that was generated on top of the melt and that these elements deposited on the exposed polished iron surface;

[0055] FIG. 6 presents examples of different amounts of gas that can be generated in aluminum alloys for different additives at different temperatures. The base system for calculations is Al+0.02% S+0.02% Al₂O₃. The dashed line represents the inferior limit of the amount of gas that should be obtained to provide a protective atmosphere which is defined as three times the initial volume of melt to be treated. In these examples, the minimum amount of additive to be added varies according to the nature of the additive and the temperature of the melt. For instance, Na cannot generate enough gas if the melt is at a temperature of about 800 Celsius, regardless of the amount that is added. However, if the temperature of the melt is increased to about 900 Celsius, the minimum amount of Na is about 0.32 wt. % to generate at least three times the initial volume of melt to be treated. For K, the minimum amount is 0.36 wt. % if the melt is at 800 Celsius, and 0.26 wt. % if the melt is at about 900 Celsius. If a mixture of half Na and half K is used in an aluminum melt at 900 Celsius, the minimum amount of Na+K will be about 0.29 wt. % (0.16 wt. % Na and 0.13 wt. % K). FIG. 7 presents examples of the minimum amount of different additives to be added to a titanium melt at 1800 Celsius. For instance, an addition of 0.11 wt. % Ca will provide about the same minimum amount of gas protection as an addition of 0.48 wt. % Zn. Similarly, FIGS. 8 to 13 present other examples of the minimum amount of different additives in different systems (Co, Cr, Cu, Fe, Mn, and Ni). FIG. 14 presents the calculated minimum amount of additive (K+Li) in a complex cobalt alloy.

[0056] After adding the at least one additive to the melted base metal material, the melt can be either atomized or cast. Water atomization is oftentimes preferred to gas atomization because it is three to nine times less expensive and is even less expensive than the other atomization processes. However, for some alloys that are readily oxidized, gas atomization is preferred. An additive treatment before gas atomization could allow improved conditions for atomization such as larger gas pressures and still achieve round particles and could also limit the amount of internal oxides and porosities. In addition, the added additive(s) can increase the sphericity of the water atomized particles, such that the sphericity approaches the sphericity of gas atomized particles.

[0057] As discussed above, the additive(s) is added in an amount such that the total volume of gas after the introduction of the additive(s) is at least three times the initial volume of the melt to be treated. In one example embodi-

ment, the additive, in this case, Mg, is added in a single operation as lumps of pure Mg in an amount ranging from 0.05 to 1.0 wt. %, for example 0.18 wt. %, based on the total weight of the melted base metal material (an iron-rich alloy) and the added magnesium. Thus, the resulting atomized powder metal material or casting includes a very low amount of residual magnesium and a total sulfur content similar to the material without the additive but for which S is now chemically bounded with the additive (as solid precipitates of MgS) and not dissolved in the melt, which leads to a larger surface tension and thus more spherical particles, and/or more spherical microstructural phases and constituents, and/or a lower amount of internal porosities. Thermodynamical calculations showed that the free sulfur content in the Mg-treated iron-rich material was more than 10 times lower than that of the non-treated material, even if the total sulfur content for both material was similar.

[0058] The additive(s) can be added in a single continuous step, for example up to 1.0 wt. % in a single continuous step, or multiple steps spaced from one another by a period of time, for example three or four steps each including up to 0.2 wt. % of the additive(s). The additive(s) can also or alternatively be added in the furnace or in a ladle and they can be in the form of pure metal, or as an alloy or compound including the additive(s). Different techniques that are already available can be used to introduce the additive(s) to the melted metal materials such as, but not limited to, lumps/chunks of the material that contain the additive(s) can be directly deposited on top of the melt or at the bottom of the furnace/crucible, or in the mold, or introduced in the melt by the usage of the cored wire technique or the usage of the plunger process. For instance, the cored wire technique uses a steel sheath filled with the Mg-rich alloy and is introduced in the melt at a rate dependent on the process parameters. The plunger technique uses a container in which the Mg containing master alloy is located, this container is plunged into the liquid cast iron. Therefore, magnesium makes contact with the liquid cast iron deeper into the melt, away from the surface.

[0059] As stated above, by adding the additive(s) to the melted metal material (in the case of Mg in Fe-rich alloys), the number of water atomized particles that have a circularity and a roundness value of 0.6 and larger increased by at least 8%, compared to the same water atomized material without the additive(s). The additive(s), for example magnesium, also results in fewer internal oxides, and could close the interface of residual oxide bifilms present in the melted metal material. This, in turn, produces cleaner atomized particles and cleaner castings having less and smaller internal porosities.

[0060] After the atomization or casting step, the method can include a post heat treatment process. The heat treating step can include annealing or another heating process typically applied to powder metal materials. The heat treatment can be conducted in an inert or reducing atmosphere, such as but not limited to an atmosphere including nitrogen, argon, and/or hydrogen or vacuum. For example, annealing in a reducing atmosphere after water atomization can reduce surface oxides. The heat treatment step can also be used to form new microstructural phases and/or constituents in the atomized particles or castings, for example graphite precipitates or nodules, carbides, or nitrides. Other microstructural phases and/or constituents could be present, depending on the composition of the metal material. In one example

embodiment, the metal material is a hypereutectic cast iron alloy, and the cementite present in the cast iron alloy transforms into ferrite and spheroidal graphite nodules during the heat treatment step, see FIGS. 17 and 18. Spherical carbides should also be formed during the heat treatment of highly alloyed steel. An external protective atmosphere or vacuum system can also be used together with the self-generated protective atmosphere described herein such as, but not limited to: the projection of a flow of nitrogen (N₂), or the projection of an argon (Ar) stream on top of the melt. The melt could also be enclosed in a chamber with a protective inert atmosphere or a vacuum system. These systems can increase the effectiveness of the process.

[0061] The additive(s) can also increase the sphericity of the microstructural constituents and/or phases formed in the atomized particles or castings during post heat treatment. However, rounder phases and/or constituents could be present in the powder metal material directly after atomization or in the as-cast materials and not only after heat treatments. The microstructural phases can include graphite precipitates, carbides, and/or nitrides. Other microstructural phases and/or constituents could be present, depending on the composition of the metal material. Typically, the microstructural constituents and/or phases have a median of the circularity and a median of the roundness of at least 0.6. Also, there is at least 10% more, and preferably at least 15% more constituents and/or phases formed in the magnesium-treated iron-based material that have a circularity and a roundness value larger than 0.6 compared to those of the same alloy but without the additive treatment.

[0062] According to one example embodiment, the powder metal material includes iron, such as cast iron, in an amount of at least 50 wt. %, and the atomized particles include graphite precipitates, wherein at least 50% of the graphite precipitates have a circularity and a roundness value of 0.6 and greater. In another embodiment, wherein the metal material is iron-based and was treated with Mg, the annealing step includes producing graphite precipitates or nodules, and the graphite precipitates or nodules have a median of the circularity and a median of the roundness of at least 0.6. In one example embodiment, the metal material is a hypereutectic cast iron alloy treated with Mg, and spheroidal graphite nodules are formed during the heat treatment process.

[0063] As stated above, the self-generated protective atmosphere created after the introduction of the additive(s) will inhibit the oxidation of the surface of the melt and will limit the amount of internal oxides in powders after atomization and in castings after solidification. FIG. 15 shows primary graphite nodules in a hypereutectic cast iron powder that precipitated on silicon oxides in suspension in the melt that were formed during pouring from the crucible to the tundish; this alloy was not treated with any additives. In Fe-rich systems that contain a high carbon content, carbon provides a protection against oxidation of the melt in the crucible (because of the high temperature), which prevents the formation of oxides in the crucible. Numerous graphite nodules that grew on these different oxides can be observed in the powder without an additive. By comparison, FIG. 16 presents one of the relatively few primary graphite nodules that can be observed in the hypereutectic cast iron powder that was treated with an additive (Mg). Since the protective atmosphere made of Mg gas limited the oxidation of the melt directly from the crucible and throughout pouring, the

amount of oxides that were present in the melt before the introduction of the additive was significantly less than in the melt without the additive. Thus, very few substrates were available for graphite precipitation during solidification and fewer graphite nodules are present.

[0064] As stated above, the melted metal material can be atomized to form a powder metal material or cast to form a solidified part. The powder metal material is typically formed by water or gas atomization, however another atomization process can be used. Powders and castings obtained with the disclosed method can be used in various different automotive or non-automotive applications. For example, the atomized particles can be used in typical press and sinter processes. The atomized particles can also be used for metal injection molding, thermal spraying, and additive manufacturing applications such as three-dimensional printing, electron beam melting, binder jetting and selective laser sintering.

[0065] When the melted metal material is cast, the method includes melting the base metal material, and then adding the at least one additive to the base metal material. The method then includes pouring the melted metal material into a mold having a desired shape, and allowing the liquid metal to solidify before removing the solidified metal part from the mold.

[0066] Experiment

[0067] FIGS. 17 and 18 are photomicrographs illustrating the improved sphericity of the microstructural phases and/or constituents, specifically graphite nodules, achieved by adding an additive (in this case magnesium) before or during the water atomization process and after heat treatment. Each material is a cast iron powder including about 4.0 wt. % carbon and 2.3 wt. % silicon. However, the material of FIG. 17 was atomized without the added magnesium, while the material of FIG. 18 was atomized with the added magnesium. The median of the roundness of the graphite nodule shown in FIG. 17, without the added magnesium, was calculated to be 0.56. The median of the roundness of the graphite nodule with magnesium shown in FIG. 18, was calculated to be 0.73. Other results that show the improved sphericity of the nodules by the additive treatment are presented in FIGS. 19 to 22.

[0068] FIGS. 23 and 24 illustrate the lower internal porosities content according to an example embodiment of the invention. In this example 304 stainless steels were water atomized. The powder presented in FIG. 24 was treated with Mg and showed a lower amount of internal porosities.

[0069] FIGS. 25 and 26 illustrate the lower internal porosities content according to an example embodiment of the invention. In this example high carbon steels alloyed with silicon were water atomized. The powder presented in FIG. 26 was treated with Mg and showed a lower amount of internal porosities.

[0070] FIG. 27 presents the chemical composition of the example embodiments of the invention.

[0071] Obviously, many modifications and variations of the present invention are possible in light of the above teachings and may be practiced otherwise than as specifically described while within the scope of the following claims. In particular, all features of all claims and of all embodiments can be combined with each other, as long as they do not contradict each other.

What is claimed is:

1. A method of manufacturing a powder metal material, comprising the steps of:

adding at least one additive to a melted base metal material, the at least one additive forming a protective gas atmosphere surrounding the melted base metal material which has a volume of at least three times greater than the volume of the melted base metal material to be treated; and

atomizing the melted base metal material after adding at least some of the at least one additive to produce a plurality of particles.

2. The method of claim 1, wherein the melted base metal material is iron-based, and the at least one additive includes magnesium.

3. The method of claim 1, wherein the atomizing step includes water atomizing, gas atomizing, plasma atomizing, ultrasonic atomization or rotating disk atomizing.

4. The method of claim 1, wherein the melted base metal material includes at least one of aluminum (Al), copper (Cu), manganese (Mn), nickel (Ni), cobalt (Co), iron (Fe), titanium (Ti), and chromium (Cr); and the melted base metal material optionally contains at least one alloying element selected from the group consisting of silver (Ag), boron (B), barium (Ba), beryllium (Be), carbon (C), calcium (Ca), cerium (Ce), gallium (Ga), germanium (Ge), potassium (K), lanthanum (La), lithium (Li), magnesium (Mg), molybdenum (Mo), nitrogen (N), sodium (Na), niobium (Nb), phosphorus (P), sulfur (S), scandium (Sc), silicon (Si), tin (Sn), strontium (Sr), tantalum (Ta), vanadium (V), tungsten (W), yttrium (Y), zinc (Zn), and zirconium (Zr).

5. The method of claim 4, wherein the at least one additive includes at least one of K, Na, Zn, Mg, Li, Sr, Ca, and Ba.

6. The method of claim 4, wherein the melted base metal material is iron-based, and the at least one additive forming the protective gas atmosphere includes at least one of K, Na, Zn, Mg, Li, Sr, and Ca.

7. The method of claim 4, wherein the melted base metal material is iron-based and includes sulfur present as an impurity; and the at least one additive includes at least one of Zn, Mg, Li, Sr, Ca, and Ba.

8. The method of claim 4, wherein the melted base metal material is iron-based and includes at least one oxide present as an impurity; and the at least one additive includes at least one of K, Na, Zn, Mg, Li, Sr, Ca, and Ba.

9. The method of claim 4, wherein the melted base metal material is iron-based and includes sulfur and at least one oxide present as impurities; and the at least one additive forming the protective gas atmosphere includes at least one of Zn, Mg, Li, Sr, and Ca.

10. The method of claim 4, wherein the melted base metal material is an aluminum alloy and includes sulfur and/or at least one oxide present as impurities; the at least one additive forming the protective gas atmosphere includes at least one of K and Na; and the at least one additive includes at least one of K, Na, Mg, Li, Sr, Ca, and Ba to react with the sulfur, and/or the at least one additive includes at least one of K, Na, Mg, Li, Ca to react with the at least one oxide.

11. The method of claim 4, wherein the melted base metal material is titanium-based and includes sulfur and/or at least one oxide present as impurities; the at least one additive forming the protective gas atmosphere includes at least one of Zn, Mg, Li, Ca and Ba; and the at least one additive includes at least one of K, Na, Zn, Mg, Li, Sr, Ca, and Ba

to react with the sulfur, and/or the at least one additive includes at least one of Sr, Ca, and Ba to react with the at least one oxide.

12. The method of claim **4**, wherein the melted base metal material is a cobalt alloy and includes sulfur and/or at least one oxide present as impurities; the at least one additive forming the protective gas atmosphere includes at least one of K, Na, Li and Ca; and the at least one additive includes at least one of Na, Mg, Li, Sr, Ca, and Ba to react with the sulfur, and/or the at least one additive includes at least one of K, Na, Zn, Mg, Li, Sr, Ca, Ba to react with the at least one oxide.

13. The method of claim **4**, wherein the melted base metal material is a chromium alloy and includes sulfur and/or at least one oxide present as impurities; the at least one additive forming the protective gas atmosphere includes at least one of K, Na, Zn, Mg, Li, Sr, Ca and Ba; and the at least one additive includes at least one of K, Na, Zn, Mg, Sr, Ca, and Ba to react with the sulfur, and/or the at least one additive includes at least one of K, Na, Zn, Mg, Li, Sr, Ca, and Ba to react with the at least one oxide.

14. The method of claim **4**, wherein the melted base metal material is iron-based; and

the at least one additive includes Mg.

15. A method of manufacturing a cast part, comprising the steps of:

adding at least one additive to a melted base metal material, the at least one additive forming a protective gas atmosphere surrounding the melted base metal material which has a volume of at least three times greater than the volume of the melted base metal material to be treated; and casting the melted metal material after adding at least some of the at least one additive.

16. The method of claim **15**, wherein the melted base metal material is iron-based, and the at least one additive includes magnesium.

17. The method of claim **15**, wherein the casting step includes sand casting, permanent mold casting, investment casting, lost foam casting, die casting, or centrifugal casting.

18. The method of claim **15**, wherein the melted base metal material includes at least one of aluminum (Al), copper (Cu), manganese (Mn), nickel (Ni), cobalt (Co), iron (Fe), titanium (Ti), and chromium (Cr); and the melted base metal material optionally contains at least one alloying element selected from the group consisting of silver (Ag), boron (B), barium (Ba), beryllium (Be), carbon (C), calcium (Ca), cerium (Ce), gallium (Ga), germanium (Ge), potassium (K), lanthanum (La), lithium (Li), magnesium (Mg), molybdenum (Mo), nitrogen (N), sodium (Na), niobium (Nb), phosphorus (P), sulfur (S), scandium (Sc), silicon (Si), tin (Sn), strontium (Sr), tantalum (Ta), vanadium (V), tungsten (W), yttrium (Y), zinc (Zn), and zirconium (Zr).

19. The method of claim **18**, wherein the at least one additive includes at least one of K, Na, Zn, Mg, Li, Sr, Ca, and Ba.

20. The method of claim **18**, wherein the melted base metal material is iron-based, and the at least one additive

forming the protective gas atmosphere includes at least one of K, Na, Zn, Mg, Li, Sr, and Ca.

21. The method of claim **18**, wherein the melted base metal material is iron-based and includes sulfur present as an impurity; and the at least one additive includes at least one of Zn, Mg, Li, Sr, Ca, and Ba.

22. The method of claim **18**, wherein the melted base metal material is iron-based and includes at least one oxide present as an impurity; and the at least one additive includes at least one of K, Na, Zn, Mg, Li, Sr, Ca, and Ba.

23. The method of claim **18**, wherein the melted base metal material is iron-based and includes sulfur and at least one oxide present as impurities; and the at least one additive forming the protective gas atmosphere includes at least one of Zn, Mg, Li, Sr, and Ca.

24. The method of claim **18**, wherein the melted base metal material is an aluminum alloy and includes sulfur and/or at least one oxide present as impurities; the at least one additive forming the protective gas atmosphere includes at least one of K and Na; and the at least one additive includes at least one of K, Na, Mg, Li, Sr, Ca, and Ba to react with the sulfur, and/or the at least one additive includes at least one of K, Na, Mg, Li, Ca to react with the at least one oxide.

25. The method of claim **18**, wherein the melted base metal material is titanium-based and includes sulfur and/or at least one oxide present as impurities; the at least one additive forming the protective gas atmosphere includes at least one of Zn, Mg, Li, Ca and Ba; and the at least one additive includes at least one of K, Na, Zn, Mg, Li, Sr, Ca, and Ba to react with the sulfur, and/or the at least one additive includes at least one of Sr, Ca, and Ba to react with the at least one oxide.

26. The method of claim **18**, wherein the melted base metal material is a cobalt alloy and includes sulfur and/or at least one oxide present as impurities; the at least one additive forming the protective gas atmosphere includes at least one of K, Na, Li and Ca; and the at least one additive includes at least one of Na, Mg, Li, Sr, Ca, and Ba to react with the sulfur, and/or the at least one additive includes at least one of K, Na, Zn, Mg, Li, Sr, Ca, Ba to react with the at least one oxide.

27. The method of claim **18**, wherein the melted base metal material is a chromium alloy and includes sulfur and/or at least one oxide present as impurities; the at least one additive forming the protective gas atmosphere includes at least one of K, Na, Zn, Mg, Li, Sr, Ca and Ba;

and the at least one additive includes at least one of K, Na, Zn, Mg, Sr, Ca, and Ba to react with the sulfur, and/or the at least one additive includes at least one of K, Na, Zn, Mg, Li, Sr, Ca, and Ba to react with the at least one oxide.

28. The method of claim **18**, wherein the melted base metal material is iron-based; and the at least one additive includes Mg.

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