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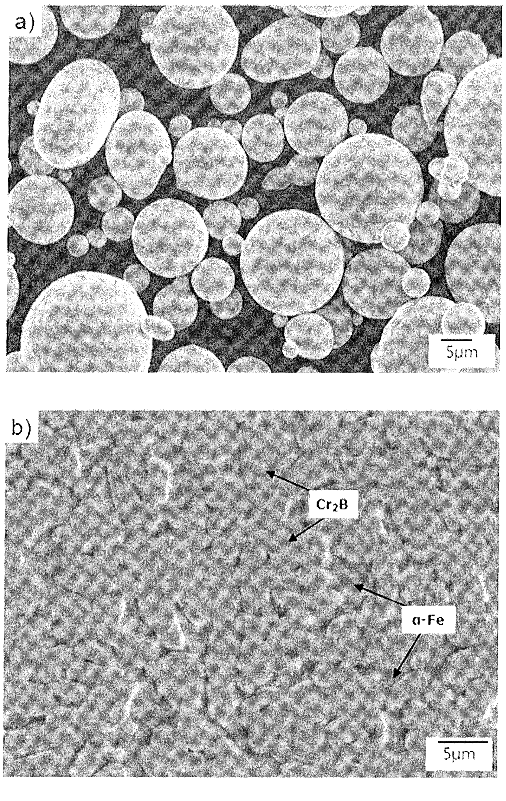
# (54) IRON-BASED ALLOY FOR POWDER INJECTION MOLDING

(57) A ferrous alloy for powder injection molding is provided. The ferrous alloy for powder injection molding includes iron (Fe) at 52.59-78.15 wt%, chromium (Cr) at 16.45-37.34 wt%, boron (B) at 3.42-7.76 wt%, silicon (Si) at 1.64-1.92wt%, sulfur (S) at 0-0.21 wt%, carbon (C) at 0.16-0.18 wt%, and other inevitable impurities.

FIG. 1



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## Description

### [Technical Field]

**[0001]** The present invention relates to a ferrous alloy, and more particularly, to a ferrous alloy for powder injection molding.

### [Background Art]

**[0002]** Powder injection molding (PIM) is new powder metallurgy molding technology in which powder metallurgy technology and an injection molding method, which is mass production technology of a precise plastic component, are coupled.

**[0003]** A PIM process is a process of producing a component by mixing a micro-powder and a polymer binder to be a subject of flow, injecting the powder and the binder into a mold, removing the binder from the mix, and finally sintering only the powder at a high temperature.

**[0004]** Continued research and development and expanded application of powder injection molding processes are ongoing because existing component designers and users recognize the merits in that the degree of freedom of component design by a combination of a material used for powder injection molding technology and a shape thereof is high, and diversified application materials and processes having economic efficiency are being developed by research institutions and powder injection molding technology companies.

**[0005]** That is, three-dimensional precision components may be made entirely of a powder material such as a metal, a ceramic, a carbide, and an intermetallic compound, and even of a processing resistant material or a material that cannot be cast, because mass production is available with few or no post-processes, so powder injection molding technology is appropriate for economically producing high value components.

**[0006]** Stainless steel that occupies most of a metal powder injection molding market has a property of strength, hardness, abrasion resistance, and corrosion resistance that a final powder injection molding component requires with a change of chemical composition.

**[0007]** Therefore, a stainless steel powder that is used for powder injection molding variously exists as SUS304L, SUS316L, SUS430, and SUS630, and for martensite-based stainless steel powder injection molding, an additional heat treatment process is necessary.

**[0008]** Therefore, development of an alloy that can be applied to various powder injection molding components without heat treatment and with economical and various microstructures and properties while fully satisfying a property of a common powder injection molding component is requested.

**[0009]** The above information disclosed in this Background section is only for enhancement of understanding of the background of the invention and therefore it may contain information that does not form the prior art that is already known in this country to a person of ordinary skill in the art.

### [DISCLOSURE]

### [Technical Problem]

**[0010]** The present invention has been made in an effort to provide a ferrous alloy having advantages of representing superior hardness, abrasion resistance, and corrosion resistance than those of stainless steel that is used for existing powder injection molding and having a low production cost.

### [Technical Solution]

**[0011]** An exemplary embodiment of the present invention provides a ferrous alloy for powder injection molding including: iron (Fe) at 52.59-78.15 wt%, chromium (Cr) at 16.45-37.34 wt%, boron (B) at 3.42-7.76 wt%, silicon (Si) at 1.64-1.92 wt%, sulfur (S) at 0-0.21 wt%, carbon (C) at 0.16-0.18 wt%, and other inevitable impurities.

**[0012]** A ratio $X_{Cr}/X_B$ of the chromium (Cr) and boron (B) may be 1.0.

**[0013]** A sum ($X_{Cr}+X_B$) of a composition of the chromium (Cr) and the boron (B) may be 0.30 to 0.60.

**[0014]** A sum ($X_{Fe}+X_{Cr}+X_B$) of a composition of the iron (Fe), the chromium (Cr), and the boron (B) may be 0.9635.

**[0015]** In a microstructure of the ferrous alloy for powder injection molding, chromium boride ($Cr_2B$) may be distributed in a network form within a ferrite base.

**[0016]** A volume fraction of the chromium boride ($Cr_2B$) may be 51-91 %.

**[0017]** Hardness of the ferrous alloy for powder injection molding may be 600-1600 VHN.

**[0018]** Another embodiment of the present invention provides a method of injection molding a ferrous powder, the method including: providing powder of the ferrous alloy for powder injection molding; forming a powder mixture by mixing the powder of the ferrous alloy for powder injection molding and a binder; compression molding the powder mixture; removing the binder by heating the powder mixture; and sintering the powder mixture from which the binder is removed.

**[0019]** The powder mixture may be formed by mixing the powder of the ferrous alloy for powder injection molding, paraffin wax, tungsten carbide balls, and heptanes in a container and rotating the container.

### [Advantageous Effects]

**[0020]** Ferrous alloys for powder injection molding according to the present invention form hard $Cr_2B$ boride with different volume fractions, thereby greatly improving hardness and abrasion resistance, compared with a conventionally used stainless steel.

**[0021]** Further, ferrous alloys for powder injection molding according to the present invention are cheaper in alloy price than a commercial stainless steel by lowering a fraction of an alloy element, and by reducing production cost by lowering a sintering temperature and reducing sintering time, the ferrous alloys are superior in price competitiveness.

### [Description of the Drawings]

**[0022]**

FIG. 1 shows scanning electron microscope (SEM) photographs illustrating a microstructure of a ferrous alloy for powder injection molding according to an exemplary embodiment of the present invention.

FIG. 2 shows Fe-Cr-B ternary system isothermal phase diagrams of a ferrous alloy that is designed according to an exemplary embodiment of the present invention.

FIG. 3 shows graphs illustrating calculation results of a precipitation driving force change of $Cr_2B$ according to each component composition on a constituent element (Fe, Cr, B, Si, S, and C) basis of a basic alloy when designing a ferrous alloy according to an exemplary embodiment of the present invention.

FIG. 4 shows graphs illustrating a fraction of equilibrium phases existing at 1000 °C according to a ratio of chromium and boron in a ferrous alloy according to an exemplary embodiment of the present invention.

FIGS. 5 to 7 show graphs illustrating an equilibrium phase fraction according to a temperature of an alloy composition of 9 ferrous alloys that are designed according to an exemplary embodiment of the present invention.

FIGS. 8 to 10 show SEM photographs of microstructures after ferrous alloys are cast and heated according to an exemplary embodiment of the present invention.

FIG. 11 illustrates X-ray diffraction analysis results of ferrous alloys according to an exemplary embodiment of the present invention.

FIG. 12 is a graph illustrating a price of an alloy element according to a property (hardness reference) that is requested for components.

### [Mode for Invention]

**[0023]** These and other objects of the present application and a method of obtaining them will become more readily apparent from the detailed description given hereinafter together with the accompanying drawings. While the present invention may be embodied in many different forms, specific embodiments of the present invention are shown in drawings and are described herein in detail, with the understanding that the present invention is to be considered as an exemplification of the principles of the invention and is not intended to limit the invention to the specific embodiments illustrated.

**[0024]** Hereinafter, a ferrous alloy for powder injection molding according to an exemplary embodiment of the present invention will be described with reference to the accompanying drawings. For reference, detailed descriptions of well-known functions and structures incorporated herein may be omitted to avoid obscuring the subject matter of the present invention.

**[0025]** It is characterized that a ferrous alloy for powder injection molding according to an exemplary embodiment of the present invention includes iron (Fe) at 52.59-78.15 wt%, chromium (Cr) at 16.45-37.34 wt%, boron (B) at 3.42-7.76 wt%, silicon (Si) at 1.64-1.92wt%, sulfur (S) at 0-0.21 wt%, carbon (C) at 0.16-0.18 wt%, and other inevitable impurities.

**[0026]** A microstructure of the ferrous alloy is characterized in that chromium boride ($Cr_2B$) is distributed in a network form within a ferrite base.

**[0027]** Because a chromium boride ($Cr_2B$) phase according to the present invention is very hard, a shape and a fraction distribution state of the precipitated chromium boride phase may have a direct influence on entire hardness and abrasion resistance of a specimen.

**[0028]** Because a chromium boride phase of the ferrous alloy forms a network structure, an entire hardness distribution of the specimen is uniform according to a position, and an applied load in an abrasion environment is distributed to be superior in an abrasion resistance property.

**[0029]** Further, it is characterized in that a volume fraction of the chromium boride ($Cr_2B$) is 51-91 %.

**[0030]** It is characterized that hardness of the alloy is 600-1600 VHN.

**[0031]** In order to satisfy a condition of high hardness and a low cost of the ferrous alloy that is requested in a powder injection molding process, a high hardness property can be obtained using precipitation of chromium boride, which is a compound of Cr and B of a relatively cheap price.

**[0032]** A composition ratio of chromium (Cr) and boron (B) is fixed to 1:1, and the sum (the sum of a mole fraction) of a composition ratio of chrome (Cr) and boron (B) may be adjusted to 0.30-0.60. In this case, the sum of a composition ratio (the sum of a mole fraction) of iron (Fe), chromium (Cr), and boron (B), which are major components, may be fixed to 0.9634.

**[0033]** The chromium (Cr) is generally an alloy element that is added to increase hardenability of the alloy and to improve corrosion resistance when quickly cooling, and in the present invention, by bonding to boron (B), the chromium (Cr) is an element that adjusts the chromium boride precipitation fraction.

**[0034]** When a content of chromium is 16.45 wt% or more, a precipitation fraction of chromium boride is formed to be 50 vol% or more, and thus hardness of about 600 VHN or more, which is a high hardness request value required in a powder injection molding process, can be obtained.

**[0035]** When a content of chromium exceeds 37.34 wt%, excessive chromium boride is precipitated and thus toughness is deteriorated, so content thereof is limited to 16.45-37.34 wt%.

**[0036]** A content of boron (B) is determined to be 3.42-7.76 wt% according to such chromium (Cr) content.

**[0037]** Boron (B) is an element that is added for improving hardenability, and in the present invention, boron (B) is an element that adjusts a chromium boride precipitation fraction by bonding to chromium. When a content of boron is 3.42 wt% or more, a precipitation fraction of chromium boride becomes 50 vol% or more, and thus hardness of about 600 VHN or more, which is a high hardness request value required in a powder injection molding process, can be obtained.

**[0038]** When a content of boron exceeds 7.76 wt%, excessive chromium boride is precipitated and thus toughness is deteriorated, so content thereof is limited to 3.42-7.76 wt%. A content of chromium is determined to be 16.45-37.34 wt% according to such content of boron.

**[0039]** In the present invention, silicone (Si) is an element that performs a function of stabilizing a base with ferrite in a sintering press of a powder injection molding process and improving hardenability through solid solution reinforcement. When a content of silicone is 1.64 wt% or less, a solid solution reinforcement and ferrite stabilization effect is slight, and when a content of silicone is 1.92 wt% or more, a solid solution reinforcement effect does not increase in proportion thereto, and so content of silicone is limited to 1.64-1.92 wt%.

**[0040]** Because sulfur generally forms a non-metallic inclusion and deteriorates properties of an alloy, it is preferable to control sulfur content to be as low as possible, but by adding sulfur up to a limit at which a sulfide (FeS) is not formed, the present invention attempts to obtain a base and chromium boride stabilization effect. Therefore, it is preferable that an upper limit thereof is set to 0.21 wt%.

**[0041]** Carbon (C) is an element that can efficiently improve hardenability of an alloy, and in order to satisfy hardness that the present invention desires, carbon (C) at 0.16 wt% or more should be contained, and when carbon (C) at 0.18 wt% or more is added, toughness is deteriorated and thus the content of carbon (C) is limited to 0.16-0.18 wt%.

**[0042]** A method of injection molding a ferrous powder according to another exemplary embodiment of the present invention includes steps of: providing a powder of a ferrous alloy for powder injection molding; forming a powder mixture by mixing the powder of a ferrous alloy for powder injection molding and a binder; compression molding the powder mixture; removing the binder by heating the powder mixture; and sintering the powder mixture from which the binder is removed.

**[0043]** The powder mixture is formed by mixing a powder of the ferrous alloy for powder injection molding, paraffin wax, tungsten carbide balls, and heptanes in a container and rotating the container.

**[0044]** Compression molding of the powder mixture may be performed by using a press at a pressure of 100 $kgf/cm^2$ or more after charging the powder mixture into a mold.

**[0045]** The binder may be removed by raising the temperature of the compression molded powder mixture up to 500 °C at a heating rate of 2 °C/min or more and maintaining the temperature for 1 hour.

**[0046]** The sintering may be performed by charging the powder mixture from which the binder is removed into a heat treating furnace, heating it to 1175 °C at a heating rate of 3 °C/min or more in a hydrogen atmosphere, and maintaining the temperature for 1 hour.

**[0047]** The present invention provides a ferrous alloy with high hardness and at a low cost for powder injection molding that may represent various properties by forming chromium boride ($Cr_2B$) of different volume fractions in a ferrite base by reducing a ratio of an alloy element and changing a ratio of chromium (Cr) and boron (B) based on a Fe-43Cr-5.6B-1.8Si-0.2S-0.17C (wt%) alloy.

**[0048]** Further, a microstructure of alloys according to the present invention may have a structure in which other crystalline particles are distributed in addition to chromium boride ($Cr_2B$) and a ferrite base.

**[0049]** Hereinafter, the present invention will be described in detail through a description of exemplary embodiments of the present invention and comparative examples. However, the following exemplary embodiments are merely examples for aiding comprehension of the present invention, and the scope of the present invention is not reduced or limited by the following exemplary embodiments.

<Exemplary Embodiment 1 >

**[0050]** Table 1 illustrates a composition of a basic alloy as a reference when designing a ferrous alloy for powder injection molding according to an exemplary embodiment of the present invention.

(Table 1)

| | Fe | Cr | B | Si | S | C |
|---|---|---|---|---|---|---|
| atomic% | Bal. 38.15 | 35.79 | 22.40 | 2.77 | 0.27 | 0.61 |
| wt% | Bal. 49.23 | 43 | 5.6 | 1.8 | 0.2 | 0.17 |

**[0051]** Table 2 illustrates a composition of an alloy in which a ferrous alloy for powder injection molding according to an exemplary embodiment of the present invention is designed by thermodynamic calculation.

(Table 2)

| Alloy | Ratio | Fe | Cr | B | Si | S | C |
|---|---|---|---|---|---|---|---|
| Exemplary Embodiment 1 | atomic % | 66.34 | 15.00 | 15.00 | 2.77 | 0.27 | 0.61 |
| | wt% | 78.15 | 16.45 | 3.42 | 1.64 | 0.18 | 0.16 |
| Exemplary Embodiment 2 | atomic % | 51.34 | 22.50 | 22.50 | 2.77 | 0.27 | 0.61 |
| | wt% | 65.54 | 26.75 | 5.56 | 1.78 | 0.20 | 0.17 |
| Exemplary Embodiment 3 | atomic % | 38.15 | 29.10 | 29.10 | 2.77 | 0.27 | 0.61 |
| | wt% | 52.59 | 37.34 | 7.76 | 1.92 | 0.21 | 0.18 |
| Exemplary Embodiment 4 | atomic % | 66.34 | 18.46 | 11.54 | 2.77 | 0.27 | 0.61 |
| | wt% | 75.86 | 19.66 | 2.55 | 1.59 | 0.18 | 0.15 |
| Exemplary Embodiment 5 | atomic % | 51.34 | 27.70 | 17.31 | 2.77 | 0.27 | 0.61 |
| | wt% | 62.49 | 31.39 | 4.08 | 1.70 | 0.19 | 0.16 |
| Exemplary Embodiment 6 | atomic % | 38.15 | 35.81 | 22.38 | 2.77 | 0.27 | 0.61 |
| | wt% | 49.22 | 43.02 | 5.59 | 1.80 | 0.20 | 0.17 |
| Exemplary Embodiment 7 | atomic % | 66.34 | 20.63 | 9.38 | 2.77 | 0.27 | 0.61 |
| | wt% | 74.50 | 21.57 | 2.04 | 1.57 | 0.17 | 0.15 |
| Exemplary Embodiment 8 | atomic % | 51.34 | 30.94 | 14.06 | 2.77 | 0.27 | 0.61 |
| | wt% | 60.72 | 34.07 | 3.22 | 1.65 | 0.18 | 0.16 |
| Exemplary Embodiment 9 | atomic % | 38.15 | 40.01 | 18.19 | 2.77 | 0.27 | 0.61 |
| | wt% | 47.33 | 46.22 | 4.37 | 1.73 | 0.19 | 0.16 |

**[0052]** A ferrous alloy for powder injection molding was arc melted under an argon (Ar) atmosphere according to a composition of Table 2. An alloy that was used for arc melting included high purity Fe (99.9 wt%), Si (99.99 wt%), and C (99 wt%), as well as previously alloyed FeB (99.2 wt%), FeS (98.5 wt%), and FeCr (98.6 wt%) as a pre-alloy, and was turned over 4-5 times and repeatedly melted so as to uniformize a mother alloy component.

**[0053]** By suction casting a mother alloy that is produced by arc melting, a bar specimen having a thickness of 5 mm was cast. Because the cast alloy is not in a homogeneous state because of sufficient diffusion, unlike a powder injection molding process product, the cast alloy was heat treated and cooled in a furnace in a similar condition (maintained for 30 min at 1200 °C) to a sintering condition of a powder injection molding process.

**[0054]** Cast and heat treated alloys were etched with a Viella solution (45 ml glycerol, 15 ml $HNO_3$, and 30 ml HCl) and were observed with a scanning electron microscope (SEM).

**[0055]** Phases existing within the alloy were analyzed with an X-ray diffraction test method, and a volume fraction of chromium boride ($Cr_2B$) was measured by an image analyzer.

**[0056]** Entire hardness of the alloy was measured under a load of 300 g by a Vickers hardness device.

<Exemplary Embodiment 2>

**[0057]** By melting element powders of a ferrous alloy for powder injection molding with a vacuum induction furnace with a 30 kg capacity according to alloy compositions of Table 2, a mother alloy ingot was produced.

**[0058]** The used alloy included high purity Fe (99.9 wt%), Si (99.99 wt%), and C (99 wt%), and previously alloyed FeB (99.2 wt%), FeS (98.5 wt%), and FeCr (98.6 wt%) as a pre-alloy.

**[0059]** The ingot was again melted at 1550 °C in an argon (Ar) atmosphere, and was produced as a spherical powder through $N^2$ gas atomization at an injection pressure of 20 bar.

**[0060]** By classifying this powder, a powder having a size of 25 μm or less was used for powder injection molding.

**[0061]** In the present invention, in order to easily mix and to reduce volume expansion, paraffin wax was used as a binder. A ferrous powder with a weight of 97 g and 3 g of a binder were mixed and charged into a high-density polyethylene (HDPE) container having a capacity of 300 ml together with 20 ml of tungsten carbide balls, and heptanes were filled to a volume of 250 ml.

**[0062]** By setting a rotation speed of the container to 45 rpm and rotating for 24 hours, the ferrous powder and the binder were mixed. After a powder mixture was dried at a hot plate at 55 °C, the powder mixture was charged into a circular mold with a diameter of 13 mm and compressed and molded using a press at room temperature with a pressure of 100 kgf/$cm^2$.

**[0063]** In order to remove the binder from the resultant compact, the temperature of the compact was raised to 500 °C at a heating rate of 2 °C/min, and the compact was maintained and degreased at this temperature for 1 hour. In order to densify the degreased compact, the compact was charged into a heat treating furnace and a temperature thereof was raised up to 1175 °C at a heating rate of 3 °C/min in a hydrogen atmosphere, and the compact was sintered for 1 hour.

<Exemplary Embodiment 3: High temperature phase equilibrium analysis by thermodynamic calculation>

**[0064]** In order to design a changed alloy composition from a basic composition of an alloy, a property determining element of the alloy is determined, and a property (particularly, hardness) of the alloy is closely related to precipitation of chromium boride ($Cr_2B$).

**[0065]** Accordingly, in order to estimate a chromium boride ($Cr_2B$) forming amount, a thermodynamic calculation was performed. Software that is used for calculation is ThermoCalc, which is a commercial thermodynamic calculation program, and as a thermodynamic database, an upgraded version of TCFE2000 was used.

**[0066]** FIG. 2 is a Fe-Cr-B ternary system isothermal phase diagram that is formed using the database.

**[0067]** FIG. 3 illustrates a calculation result of a precipitation driving force change of $Cr_2B$ according to each component composition on a constituent element (Fe, Cr, B, Si, S, and C) basis of a basic alloy at 1250 °C (pink) and 1000 °C (yellowish green).

**[0068]** A precipitation driving force is obtained by calculating an amount of a component to adjust in a range from 0 to two times an original amount in a state in which a ratio between other components is fixed.

**[0069]** It can be seen from FIG. 3 that when changing an amount of iron (Fe), chromium (Cr), and boron (B), which are major constituent elements of a basic alloy, a precipitation driving force of chromium boride ($Cr_2B$) is greatly changed. Therefore, when selecting a basic alloy for designing an alloy, iron, chromium, and boron were used as major variables.

**[0070]** When a basic alloy is used for PIM, the basic alloy is sintered for a long time at 1200 °C in a powder injection process, and thus it may be considered that a sintered microstructure has arrived at equilibrium.

**[0071]** At 1000 °C, which is a temperature that may be thought of as a cooling temperature after arriving at equilibrium, by adjusting a composition of iron, chromium, and boron, an equilibrium phase fraction was calculated.

**[0072]** A composition was obtained when the sum ($X_{Fe}$+$X_{Cr}$+$X_B$) of a mole fraction of a major component is maintained at 0.9634 based on a basic alloy of Table 1 as a reference, but values of $X_{Fe}$ and ($X_{Cr}$+$X_B$) were adjusted by setting a ratio $X_{Cr}/X_B$ of Cr and B to three cases of 1.0 (B ratio increase), 1.6 (basis ratio), and 2.2 (Cr ratio increase).

**[0073]** FIG. 4 illustrates a fraction of equilibrium phases existing at 1000 °C in the three cases. As the boron ratio increases and as the ($X_{Cr}$+$X_B$) value increases, an equilibrium phase fraction of chromium boride ($Cr_2B$) increases.

**[0074]** In a composition ratio of the three cases, by again selecting three cases of ($X_{Cr}$+$X_B$)=0.30, 0.45, and 0.5819, a total of 9 alloy compositions were obtained, and this is represented in Table 2.

**[0075]** First, at each of compositions in which an $X_{Cr}/X_B$ ratio is 1.0, 1.6, and 2.2, cases in which the ($X_{Cr}$+$X_B$) sums are 0.30, 0.45, and 0.5819 were divided into Exemplary Embodiments 1 to 9.

**[0076]** Here, Exemplary Embodiment 6 of $X_{Cr}/X_B$=1.6 and ($X_{Cr}$+$X_B$)=0.5819 is the same as an alloy of Table 1, which is a reference composition.

**[0077]** FIGS. 5 to 7 are graphs illustrating an equilibrium phase fraction according to a temperature of the 9 alloy compositions. Thereby, thermodynamic calculation values of an equilibrium phase fraction of chromium boride ($Cr_2B$) at several temperatures may be seen.

**[0078]** For example, in an alloy composition of Exemplary Embodiment 1 ($X_{Cr}/X_B$=1.0, $X_{Cr}$+$X_B$=0.30), at 1000 °C, a $Cr_2B$ fraction is about 43 vol% and the remaining elements are BCC $\alpha$-Fe (ferrite) and FCC $\gamma$-Fe (austenite). When the temperature drops to room temperature, a fraction of $Cr_2B$ is maintained, $\gamma$-Fe is transformed into $\alpha$-Fe, and thus it is expected that a room temperature microstructure is formed with $Cr_2B$ of 43 vol% and $\alpha$-Fe of 57 vol%.

<Exemplary Embodiment 4: Microstructure of ferrous alloy>

**[0079]** As long time sintering is performed at a high temperature, PIM components arrive at a sufficient equilibrium state, but after melting, because solidification by cooling occurs relatively quickly, a cast alloy may not arrive in an equilibrium state.

**[0080]** Therefore, in order to obtain a microstructure having arrived in a sufficient equilibrium state, heat treatment corresponding to a sintering process of PIM was applied to a cast alloy.

**[0081]** FIGS. 8 to 10 illustrate SEM microstructures of heat-treated alloys after casting. After heat treatment, because diffusion occurs, a microstructure thereof is considerably different from that of the cast alloy.

**[0082]** When martensite is maintained for a long time at a high temperature, the martensite is changed to tempered martensite, i.e., ferrite in which micro-carbides are precipitated, and a form of $Cr_2B$ is changed from a needle shape or a bar shape to a spherical or oval shape.

**[0083]** Like a case of a cast alloy, as ($X_{Cr}$+$X_B$) increases, a tendency that a $Cr_2B$ amount increases is represented. A microstructure (FIG. 9 (f)) of an alloy of Exemplary Embodiment 6 having the same composition as an alloy of a reference composition is similar to that of a component that is powder injection molded with the basic alloy powder of FIG. 1. It may be expected that a microstructure of a heat-treated alloy after casting will be similar to a microstructure of a component having passed through a PIM process after making the alloy into powder.

**[0084]** FIG. 11 illustrates X-ray diffraction analysis results of heat-treated alloys. Because a peak of $\alpha$-Fe (ferrite) and $Cr_2B$ is represented in all alloys, it can be seen that $Cr_2B$ is distributed within a ferrite base. A precipitated $Cr_2B$ fraction was measured and is represented in Table 3, and was compared with a $Cr_2B$ fraction that is obtained from FIGS. 5 to 7 representing an equilibrium phase fraction.

<Exemplary Embodiment 5: Hardness of ferrous alloy>

**[0085]** Hardness of a cast alloy and a heat-treated alloy was measured and is represented in Table 3. Hardness of a cast alloy and a heat-treated alloy is different in the same chemical composition because a microstructure of a cast alloy that is formed with $Cr_2B$ and martensite is changed after heat treatment.

(Table 3)

| Alloy | Volume fraction of chromium boride (vol%) | | Vickers hardness (VHN) | |
|---|---|---|---|---|
| | Calculation value | After heat treatment | After casting | After heat treatment |
| Exemplary Embodiment 1 | 48 | 51 | 1107.5 (±60.8) | 595.4 (±37.8) |
| Exemplary Embodiment 2 | 71 | 76 | 1200.5 (±7.6) | 1144.6 (±123.7) |
| Exemplary Embodiment 3 | 89 | 91 | 1649.6 (±105.1) | 1624.7 (±125.2) |
| Exemplary Embodiment 4 | 40 | 46 | 837.4 (±52.8) | 404.4 (±14.6) |
| Exemplary Embodiment 5 | 57 | 59 | 735.3 (±14.0) | 648.9 (±170.7) |
| Exemplary embodiment 6 | 71 | 80 | 759.5 (±33.4) | 1260.5 (±55.5) |
| Exemplary Embodiment 7 | 34 | 42 | 658.0 (±89.2) | 325.7 (±17.7) |
| Exemplary Embodiment 8 | 47 | 47 | 482.8 (±18.3) | 537.0 (±58.2) |
| Exemplary Embodiment 9 | 60 | 66 | 617.6 (±6.2) | 962.5 (±149.2) |

**[0086]** In the cast alloy, martensite is changed to ferrite after heat treatment, and $Cr_2B$ arrives in an equilibrium state by a diffusion effect by high temperature heat treatment and thus hardness and a fraction of $Cr_2B$ increases. After heat treatment, as martensite is changed to ferrite, hardness decreases, and as hardness and a fraction of $Cr_2B$ increases, hardness increases, while hardness of a cast alloy increases or decreases after heat treatment according to a competition relationship between the two.

**[0087]** That is, in an alloy composition having a high $Cr_2B$ fraction, an increase effect of hardness and a fraction of $Cr_2B$ is larger than a hardness decrease by martensite-ferrite transformation, and thus after heat treatment, hardness increases. However, in an alloy composition having a high ferrite fraction, because a hardness decrease effect by martensite-ferrite transformation is larger than an increase effect of hardness and a fraction of $Cr_2B$, a tendency that hardness decreases after heat treatment is represented.

**[0088]** Ferrous alloys that are produced in this research may be variously used for producing a PIM component according to a fraction and hardness of $Cr_2B$ in consideration of similarity of a microstructure (FIG. 9 (f)) of an alloy of Exemplary Embodiment 6 and a microstructure (FIG. 1) of a component in which PIM is performed with a basic alloy powder.

**[0089]** As a $Cr_2B$ fraction generally increases, hardness increases, but a brittle fracture possibility increases. Therefore, when applying to a PIM component, a high $Cr_2B$ fraction and hardness are not always necessary and thus it is preferable to effectively select an alloy having a property that is appropriate for a property that is requested for the component.

**[0090]** For example, when a hardness condition that is requested for a PIM component is 500-600 VHN, an alloy corresponding thereto, for example, alloys of Exemplary Embodiments 1, 5, and 8, may be applied. In this case, the alloy may have a merit that brittleness decreases and toughness increases, compared with an alloy having high hardness.

**[0091]** Further, when a $Cr_2B$ fraction increases, an amount of an alloy element increases according to the increased $Cr_2B$ fraction, and thus it is preferable to together consider economic efficiency including a price of an alloy element as well as a property that is requested for the PIM component.

**[0092]** FIG. 12 is a graph illustrating a price of an alloy element according to a property (hardness reference) that is requested for components. A price reference of an alloy element was formed based on an LME daily price (based on July 27, 2010).

**[0093]** A price of an alloy element that is contained in an alloy that is made in this research is lower than that of a basic alloy, and when hardness decreases, an alloy element price also decreases.

**[0094]** Further, because a price of an alloy element is lower than that of ferrite-based or martensite-based SUS630 stainless steel (composition: Fe-17Cr-4Ni-4Cu-0.35Nb-0.07C (wt%), hardness: 360 VHN) that is much used for PIM, the alloy element may be fully used as a replacement.

**[0095]** Therefore, when simultaneously considering a property and economic efficiency that is requested for a PIM component, an alloy of this research can be fully applied to a PIM component of various conditions and has an excellent property and advantageous economic efficiency.

**[0096]** As described above, as hard $Cr_2B$ adjusts a $Cr_2B$ fraction from the present invention in which a PIM alloy that is distributed in a ferrite base is designed, an alloy representing various properties may be successfully produced.

**[0097]** Particularly, a $Cr_2B$ fraction and hardness was estimated from a calculation result of a high temperature equilibrium phase fraction by a thermodynamic calculation, and a ferrous alloy having various $Cr_2B$ fractions and hardness was produced using this.

**[0098]** As these alloys contain much $Cr_2B$ that is stable at a high temperature and has excellent corrosion resistance, it is expected that these alloys are much superior to an existing stainless steel PIM component in terms of high temperature property, abrasion resistance, and corrosion resistance, as well as room temperature hardness, and thus there is a new possibility that these alloys can be applied to a structural components that require excellent properties.

**[0099]** Because an alloy of Exemplary Embodiment 3 represents hardness of 1600 VHN or more, the alloy may be fully applied even to a PIM component of a tungsten carbide alloy as well as stainless steel.

**[0100]** While this invention has been described in connection with what is presently considered to be practical exemplary embodiments, it is to be understood that the invention is not limited to the disclosed embodiments, but, on the contrary, is intended to cover various modifications and equivalent arrangements included within the spirit and scope of the appended claims.

## Claims

1. A ferrous alloy for powder injection molding, comprising iron (Fe) at 52.59-78.15 wt%, chromium (Cr) at 16.45-37.34 wt%, boron (B) at 3.42-7.76 wt%, silicon (Si) at 1.64-1.92 wt%, sulfur (S) at 0-0.21 wt%, carbon (C) 0.16-0.18 wt%, and other inevitable impurities.

2. The ferrous alloy of claim 1, wherein a ratio $X_{Cr}/X_B$ of the chromium (Cr) and boron (B) is 1.0.

**3.** The ferrous alloy of claim 2, wherein a sum ($X_{Cr}+X_B$) of a mole fraction of the chromium (Cr) and the boron (B) is 0.30 to 0.60.

**4.** The ferrous alloy of any one of claims 1 to 3, wherein a sum ($X_{Fe}+X_{Cr}+X_B$) of a mole fraction of the iron (Fe), the chromium (Cr), and the boron (B) is 0.9635.

**5.** The ferrous alloy of claim 4, wherein in a microstructure of the ferrous alloy for powder injection molding, chromium boride ($Cr_2B$) is distributed in a network form within a ferrite base.

**6.** The ferrous alloy of claim 5, wherein a volume fraction of the chromium boride ($Cr_2B$) is 51-91 %.

**7.** The ferrous alloy of claim 6, wherein hardness of the ferrous alloy for powder injection molding is 600-1600 VHN.

**8.** A method of injection molding a ferrous powder, the method comprising:

providing powder of a ferrous alloy for powder injection molding according to any one of claims 1 to 7;
forming a powder mixture by mixing the powder of the ferrous alloy for powder injection molding and a binder;
compression molding the powder mixture;
removing the binder by heating the powder mixture; and
sintering the powder mixture from which the binder is removed.

**9.** The method of claim 8, wherein the powder mixture is formed by mixing the powder of the ferrous alloy for powder injection molding according to any one of claims 1 to 8, paraffin wax, tungsten carbide balls, and heptanes in a container and rotating the container.

FIG. 1

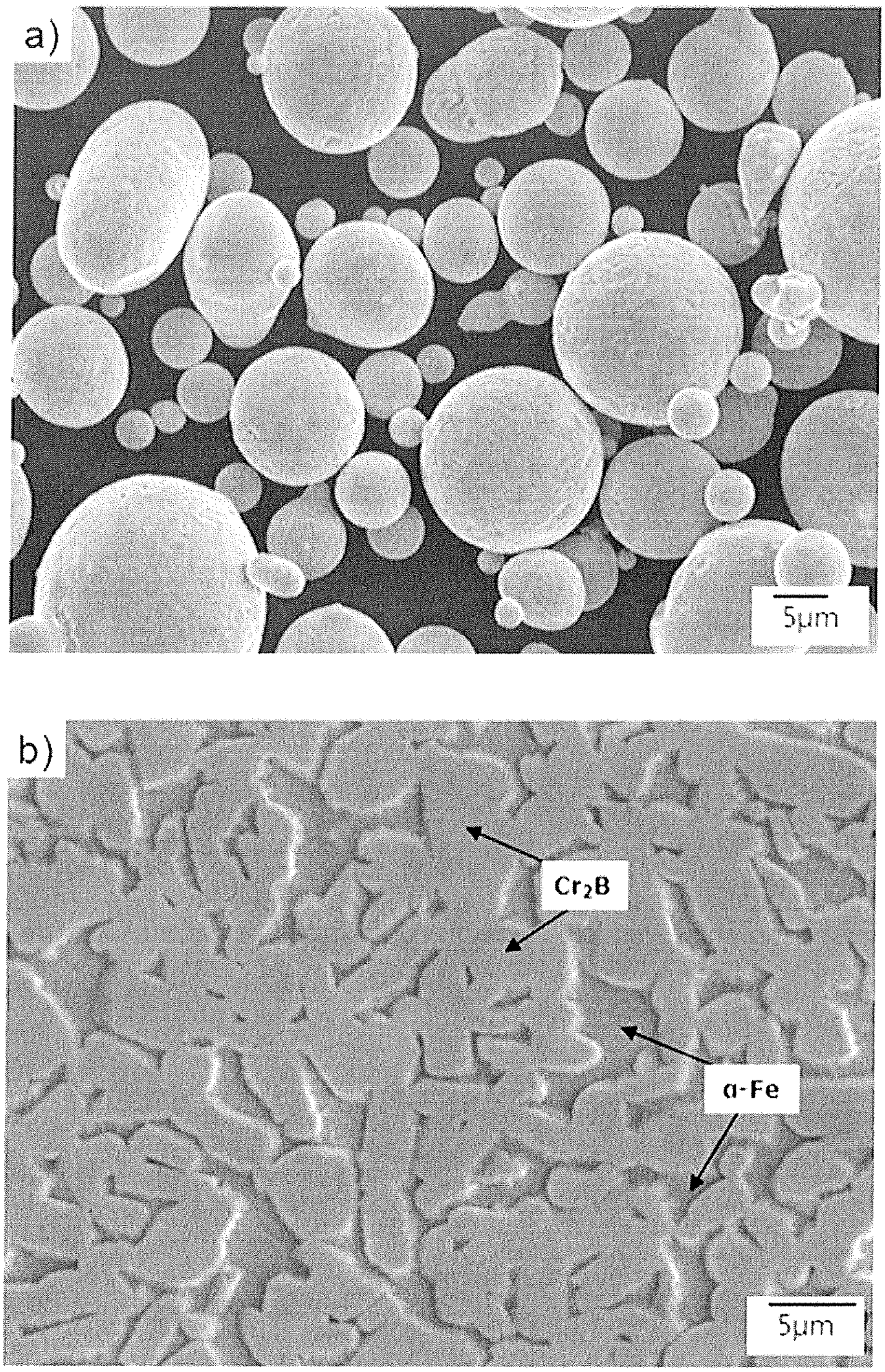


FIG. 2

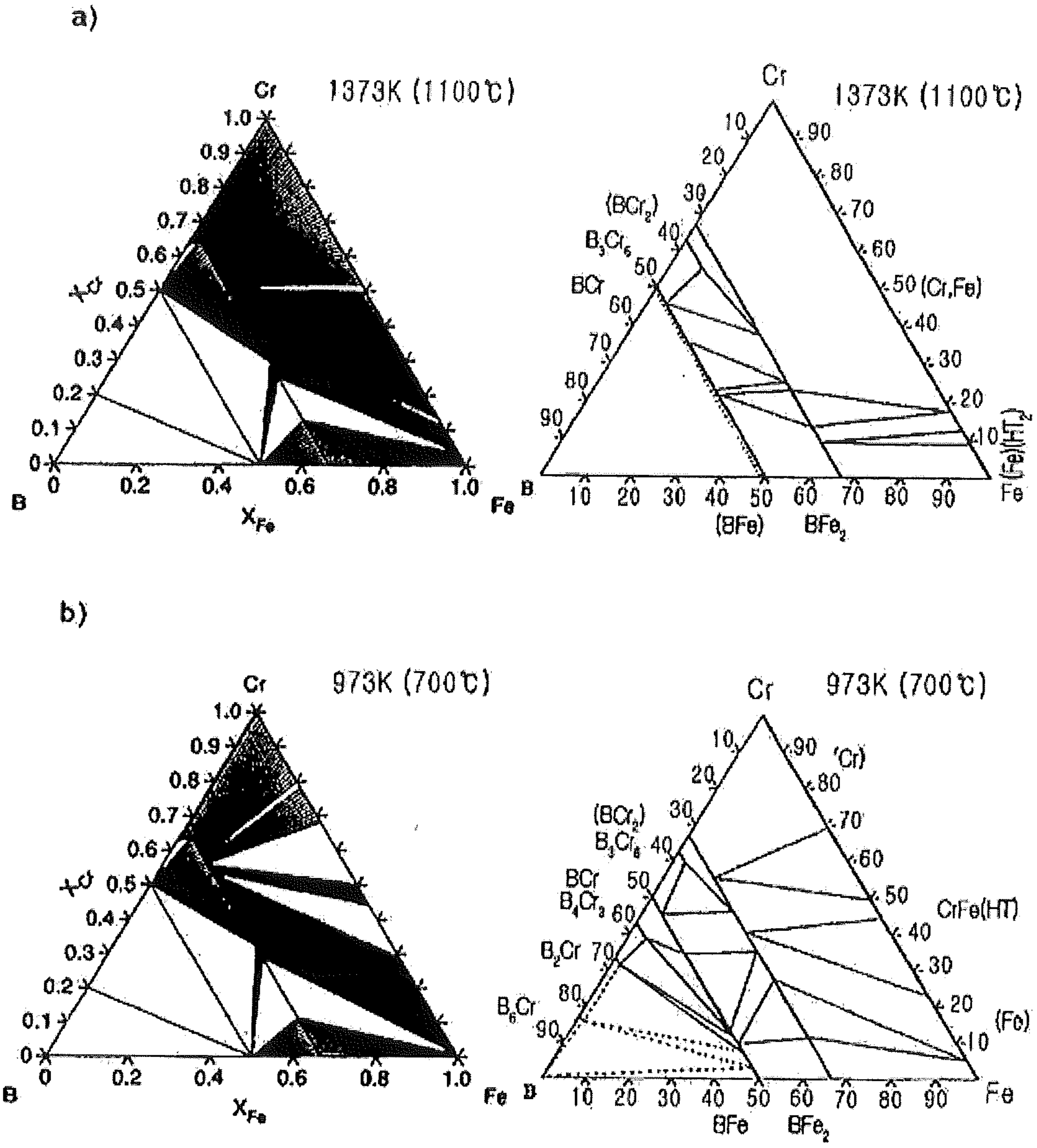

a)
Cr
1373K (1100℃)
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
B
0
0.2
0.4
0.6
0.8
1.0
Fe
$X_{Fe}$
Cr
1373K (1100℃)
10
20
30
40
50
60
70
80
90
(BCr2)
B3Cr5
BCr
90
80
70
60
50 (Cr,Fe)
40
30
20
10
(Fe)(HT)2
B
10
20
30
40
50
60
70
80
90
Fe
(BFe)
BFe2
b)
Cr
973K (700℃)
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
B
0
0.2
0.4
0.6
0.8
1.0
Fe
$X_{Fe}$
Cr
973K (700℃)
10
20
30
40
50
60
70
80
90
(BCr2)
B3Cr5
BCr
B4Cr3
B2Cr
B6Cr
90
'Cr)
80
70
60
50
CrFe(HT)
40
30
20
(Fe)
10
B
10
20
30
40
50
60
70
80
90
Fe
BFe
BFe2

FIG. 3

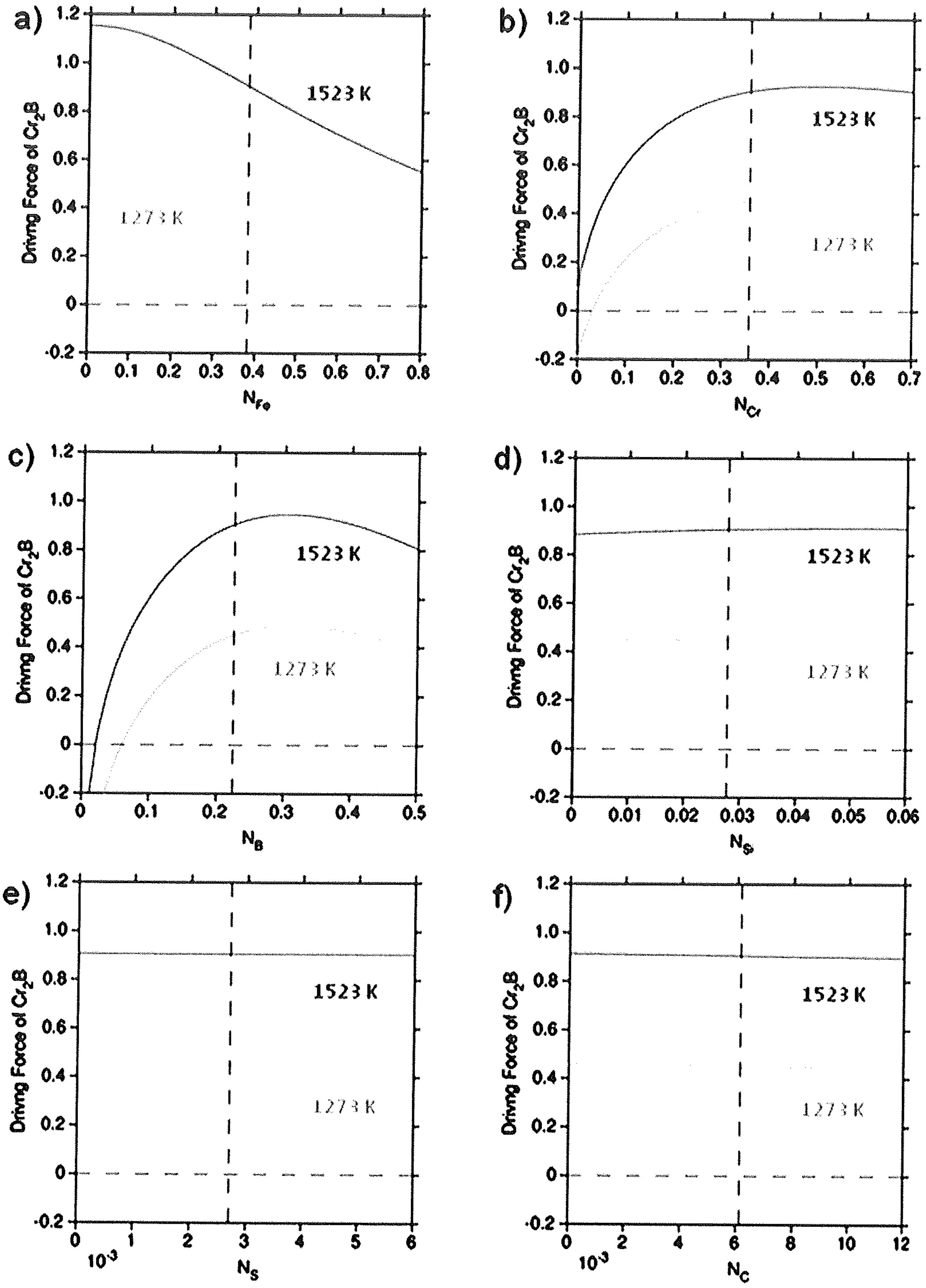

a)
Driving Force of Cr$_2$B
1.2
1.0
0.8
0.6
0.4
0.2
0
-0.2
1523 K
1273 K
0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8
$N_{Fe}$
b)
Driving Force of Cr$_2$B
1523 K
1273 K
0 0.1 0.2 0.3 0.4 0.5 0.6 0.7
$N_{Cr}$
c)
Driving Force of Cr$_2$B
1523 K
1273 K
0 0.1 0.2 0.3 0.4 0.5
$N_B$
d)
Driving Force of Cr$_2$B
1523 K
1273 K
0 0.01 0.02 0.03 0.04 0.05 0.06
$N_{Si}$
e)
Driving Force of Cr$_2$B
1523 K
1273 K
0 1 2 3 4 5 6
$10^{-3}$
$N_S$
f)
Driving Force of Cr$_2$B
1523 K
1273 K
0 2 4 6 8 10 12
$10^{-3}$
$N_C$

FIG. 4

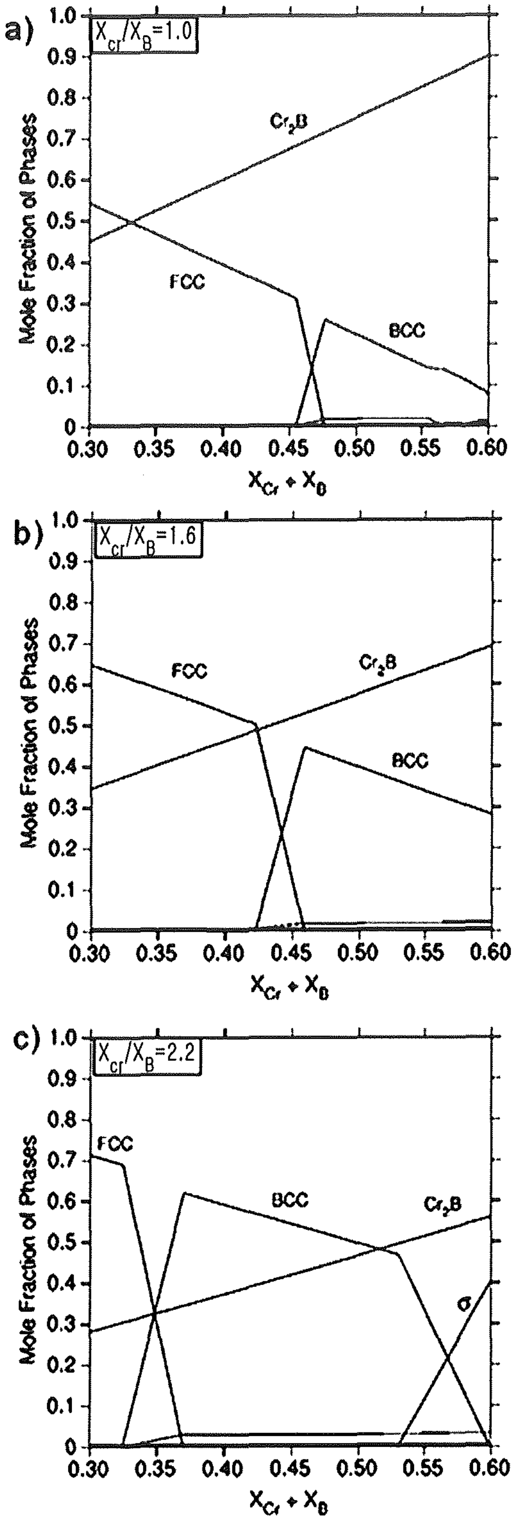

a)
$X_{Cr}/X_B$=1.0
Cr₂B
FCC
BCC
Mole Fraction of Phases
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0.30
0.35
0.40
0.45
0.50
0.55
0.60
$X_{Cr} + X_B$
b)
$X_{Cr}/X_B$=1.6
FCC
Cr₂B
BCC
Mole Fraction of Phases
$X_{Cr} + X_B$
c)
$X_{Cr}/X_B$=2.2
FCC
BCC
Cr₂B
σ
Mole Fraction of Phases
$X_{Cr} + X_B$

FIG. 5

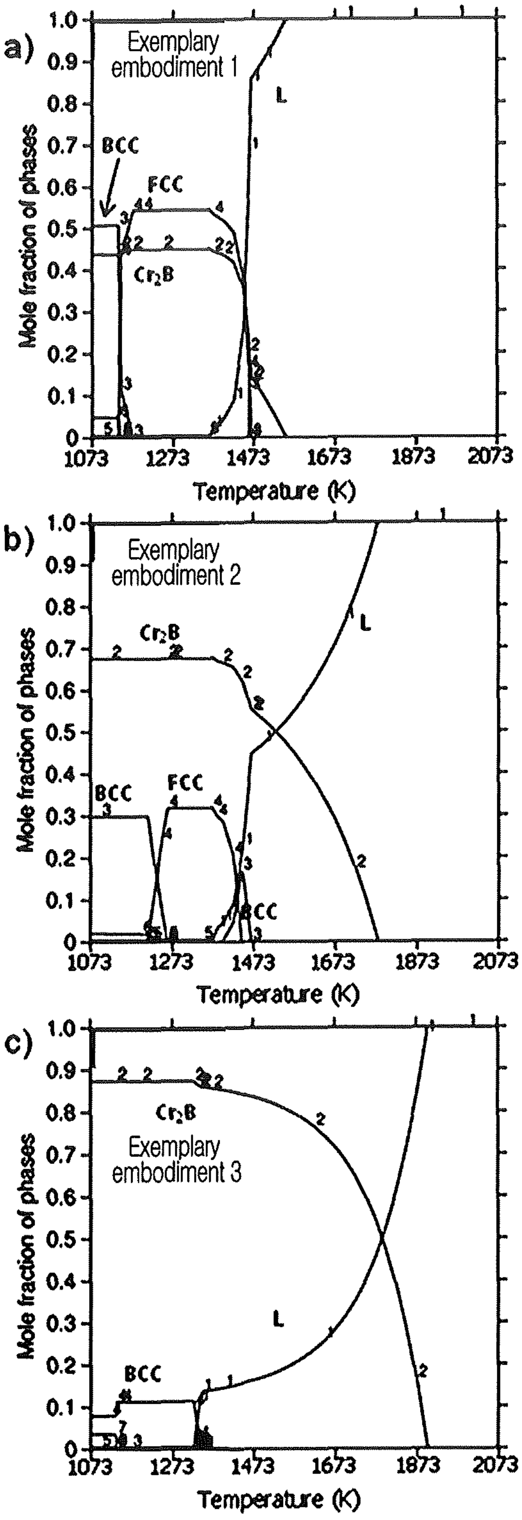

a)
Exemplary embodiment 1
BCC
FCC
Cr₂B
L
Mole fraction of phases
Temperature (K)
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
1073
1273
1473
1673
1873
2073
b)
Exemplary embodiment 2
Cr₂B
BCC
FCC
L
BCC
Mole fraction of phases
Temperature (K)
c)
Exemplary embodiment 3
Cr₂B
L
BCC
Mole fraction of phases
Temperature (K)

FIG. 6

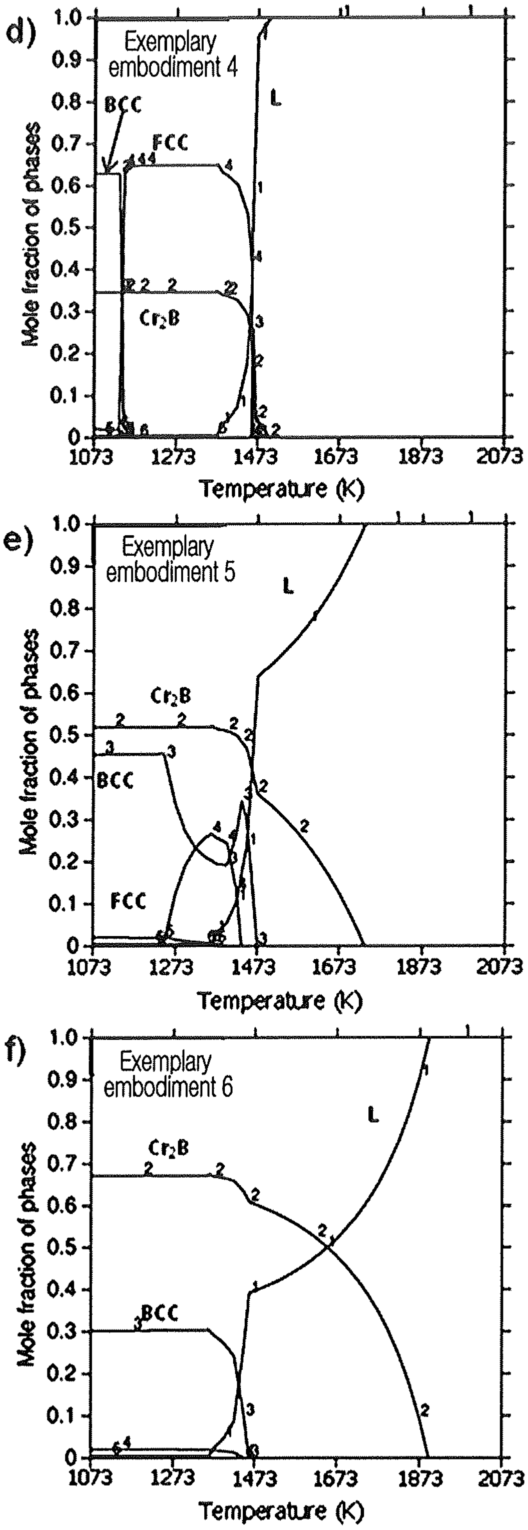

d)
Exemplary embodiment 4
BCC
FCC
Cr2B
L
e)
Exemplary embodiment 5
L
Cr2B
BCC
FCC
f)
Exemplary embodiment 6
L
Cr2B
BCC
Mole fraction of phases
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
Temperature (K)
1073
1273
1473
1673
1873
2073

FIG. 7

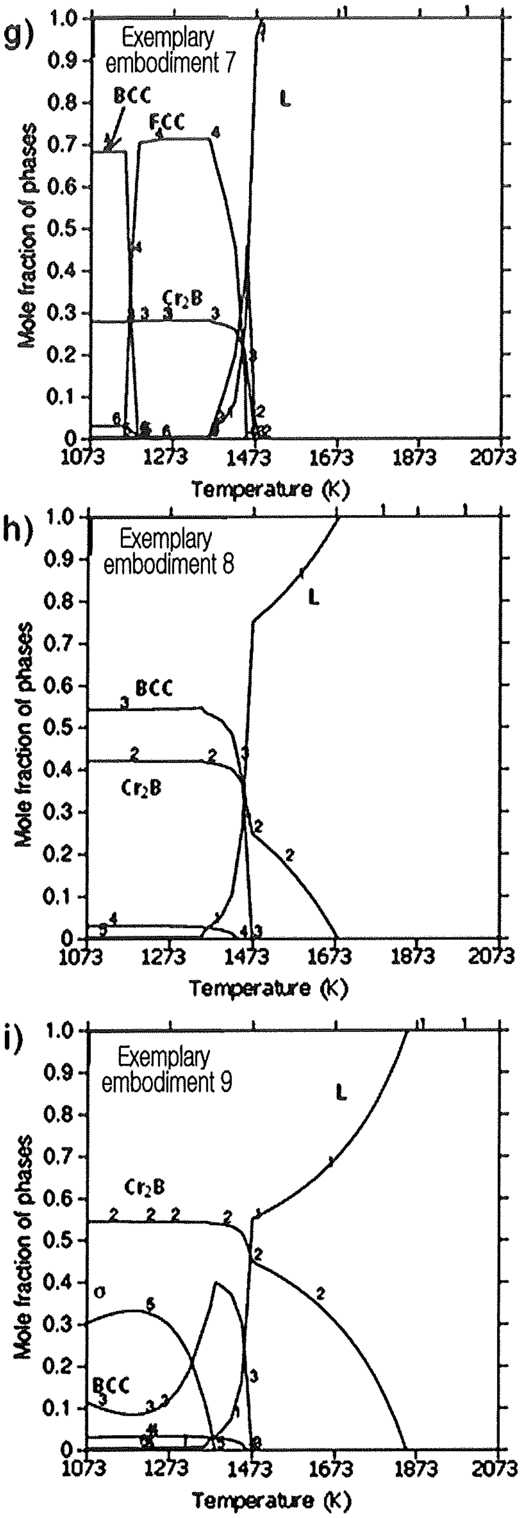

g)
Exemplary embodiment 7
BCC
FCC
Cr₂B
L
h)
Exemplary embodiment 8
BCC
Cr₂B
L
i)
Exemplary embodiment 9
Cr₂B
σ
BCC
L
Mole fraction of phases
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
Temperature (K)
1073
1273
1473
1673
1873
2073

FIG. 8

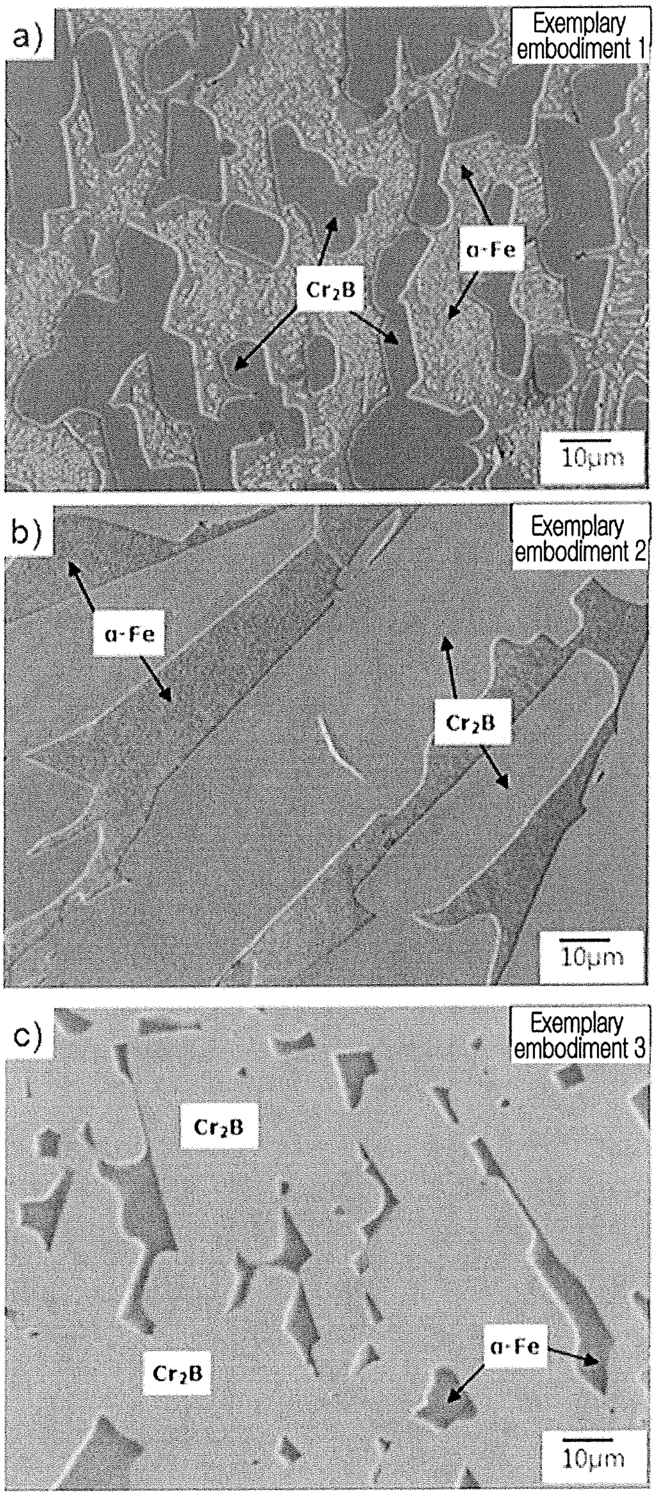

a)
Exemplary embodiment 1
α-Fe
Cr₂B
10μm
b)
Exemplary embodiment 2
α-Fe
Cr₂B
10μm
c)
Exemplary embodiment 3
Cr₂B
Cr₂B
α-Fe
10μm

FIG. 9

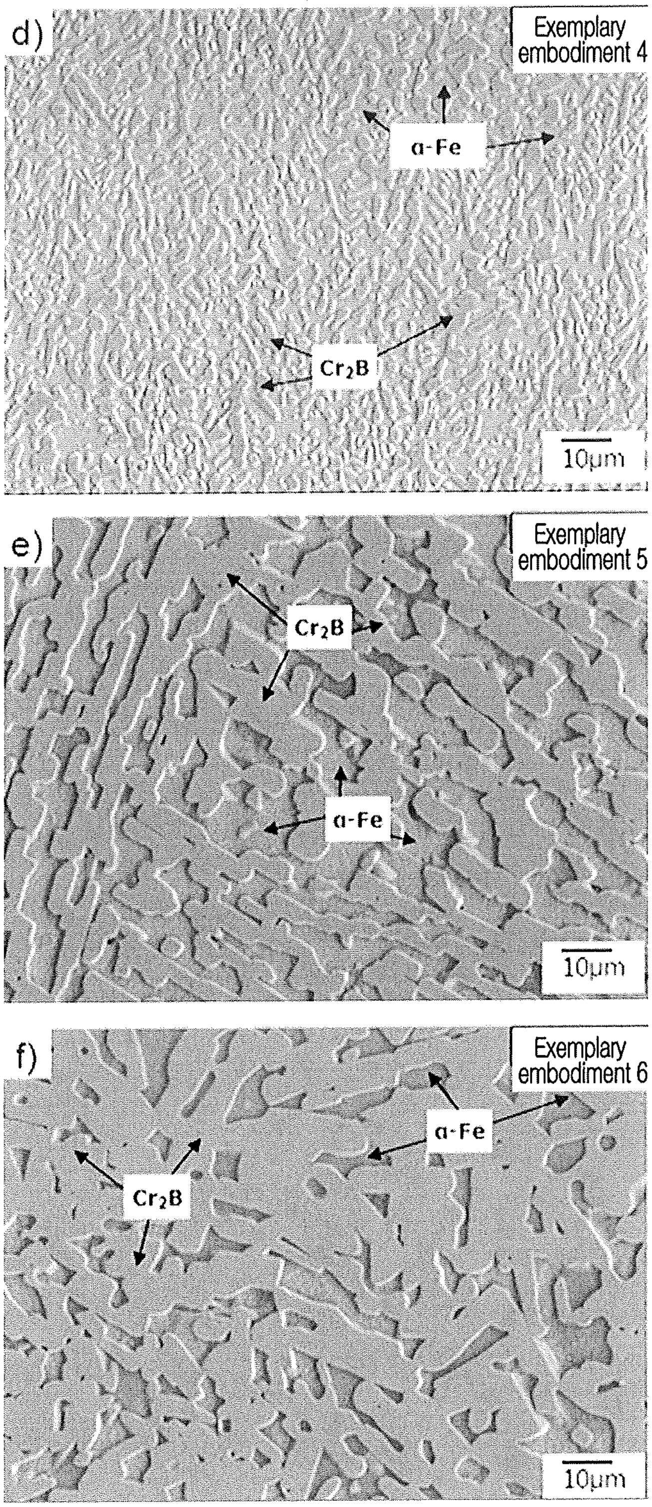

d)
Exemplary embodiment 4
α-Fe
Cr₂B
10μm
e)
Exemplary embodiment 5
Cr₂B
α-Fe
10μm
f)
Exemplary embodiment 6
α-Fe
Cr₂B
10μm

FIG. 10

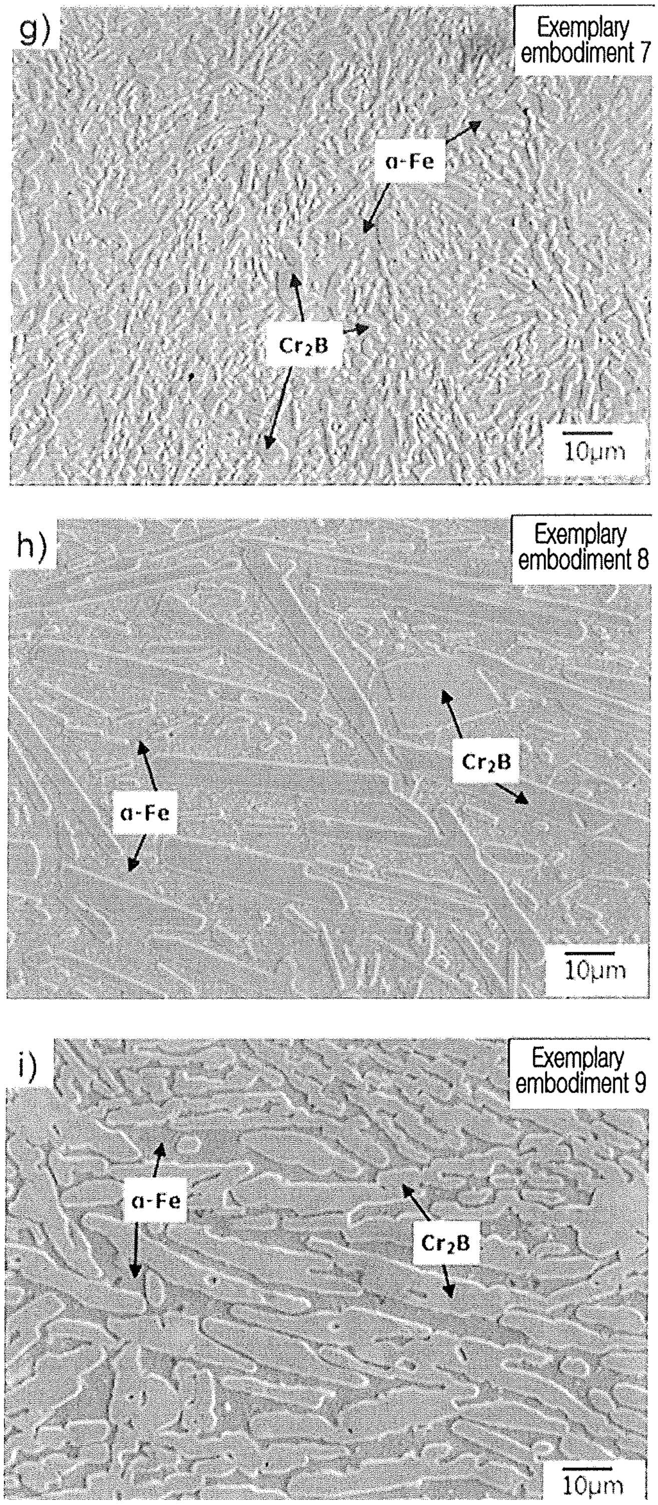

g)
Exemplary embodiment 7
α-Fe
Cr$_2$B
10μm
h)
Exemplary embodiment 8
Cr$_2$B
α-Fe
10μm
i)
Exemplary embodiment 9
α-Fe
Cr$_2$B
10μm

FIG. 11

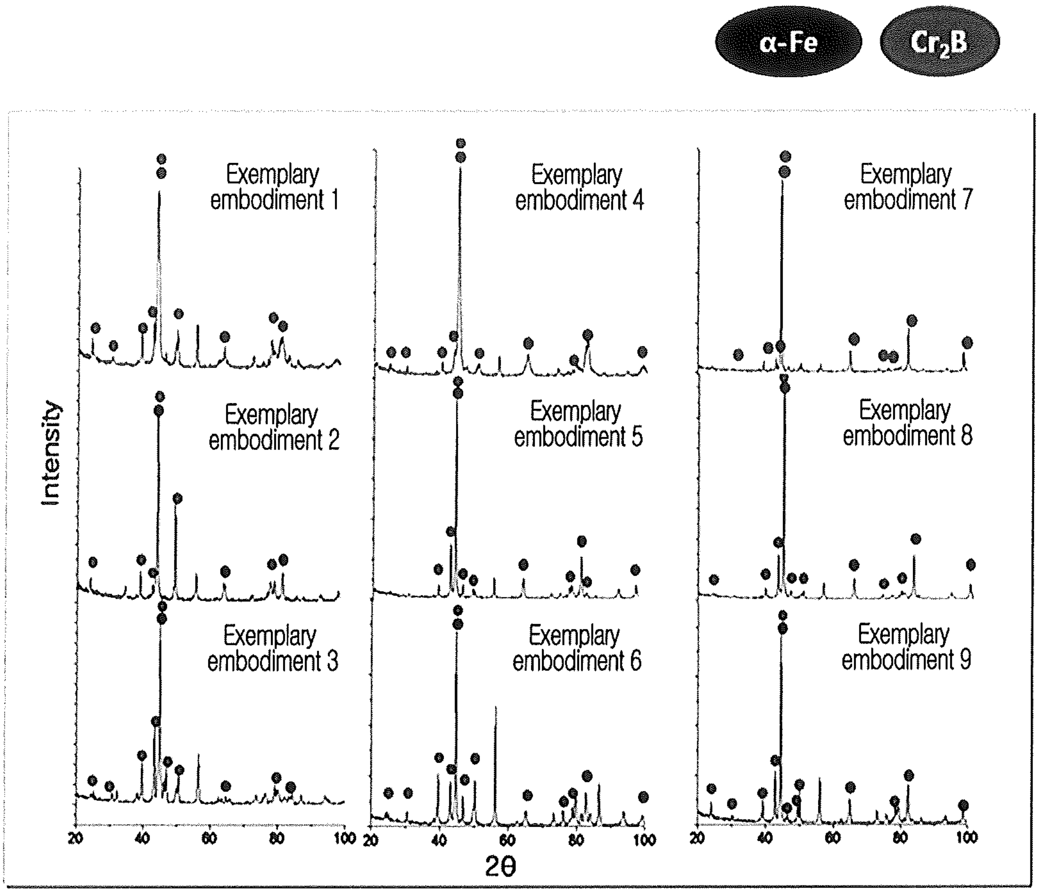
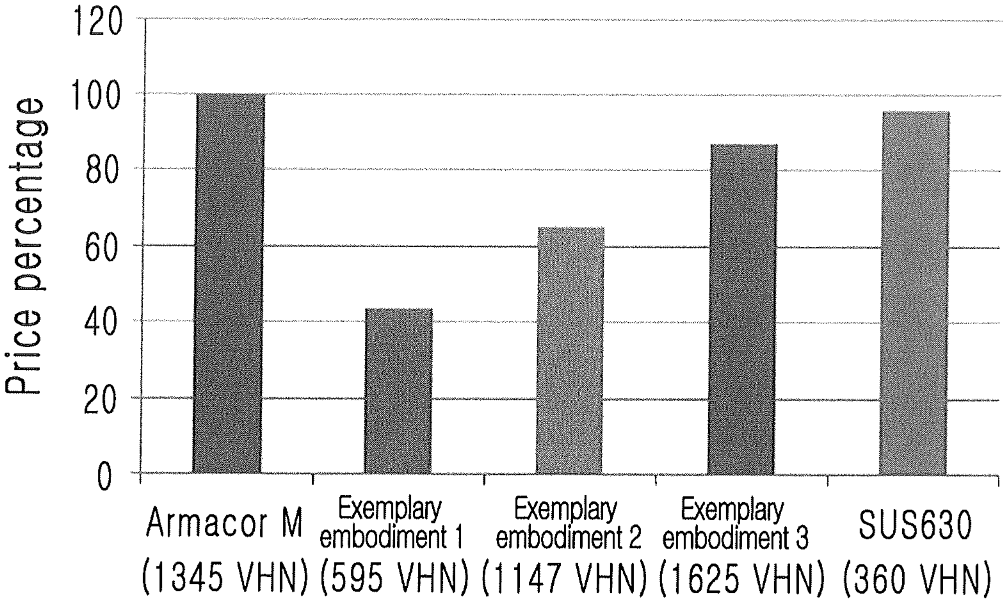

α-Fe
Cr2B
Exemplary embodiment 1
Exemplary embodiment 2
Exemplary embodiment 3
Exemplary embodiment 4
Exemplary embodiment 5
Exemplary embodiment 6
Exemplary embodiment 7
Exemplary embodiment 8
Exemplary embodiment 9
Intensity
20
40
60
80
100
2θ

FIG. 12


Price percentage
120
100
80
60
40
20
0
Armacor M (1345 VHN)
Exemplary embodiment 1 (595 VHN)
Exemplary embodiment 2 (1147 VHN)
Exemplary embodiment 3 (1625 VHN)
SUS630 (360 VHN)

## INTERNATIONAL SEARCH REPORT

International application No.
**PCT/KR2012/003071**

A. CLASSIFICATION OF SUBJECT MATTER

***C22C 38/00(2006.01)i, B22F 3/12(2006.01)i***

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)
C22C 38/00; B22F 3/115; B22F 5/00; B22F 3/00; B29C 45/00

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Korean Utility models and applications for Utility models: IPC as above
Japanese Utility models and applications for Utility models: IPC as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
eKOMPASS (KIPO internal) & Keywords: powder, injection molding, boron, chrome boride

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| A | KR 10-0768700 B1 (POSTECH FOUNDATION et al.) 19 October 2007<br>See abstract and claims 9 - 11. | 1-9 |
| A | JP 2001-234305 A (NIPPON PISTON RING CO LTD) 31 August 2001<br>See abstract and claims 1, 2. | 1-9 |
| A | KR 10-2006-0068807 A (PARK, YOUNG SUK) 21 June 2006<br>See abstract and claims 1 - 13. | 1-9 |

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

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
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"&" document member of the same patent family

| | |
|---|---|
| Date of the actual completion of the international search<br>24 OCTOBER 2012 (24.10.2012) | Date of mailing of the international search report<br>**01 NOVEMBER 2012 (01.11.2012)** |
| Name and mailing address of the ISA/KR<br>Korean Intellectual Property Office<br>Government Complex-Daejeon, 139 Seonsa-ro, Daejeon 302-701, Republic of Korea<br>Facsimile No. 82-42-472-7140 | Authorized officer<br><br>Telephone No. |

Form PCT/ISA/210 (second sheet) (July 2009)

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
**PCT/KR2012/003071**

| Patent document cited in search report | Publication date | Patent family member | Publication date |
|---|---|---|---|
| KR 10-0768700 B1 | 19.10.2007 | CN 101479063 A<br>CN 101479063 B<br>EP 2043801 A1<br>JP 2009-542905 A<br>US 2009-0297396 A1<br>WO 2008-002001 A1 | 08.07.2009<br>07.12.2011<br>08.04.2009<br>03.12.2009<br>03.12.2009<br>03.01.2008 |
| JP 2001-234305 A | 31.08.2001 | JP 3988971 B2 | 10.10.2007 |
| KR 10-2006-0068807 A | 21.06.2006 | NONE | |

Form PCT/ISA/210 (patent family annex) (July 2009)