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(54) **METAL POWDER FOR POWDER  
METALLURGY, COMPOUND, GRANULATED  
POWDER, AND SINTERED BODY**

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**ABSTRACT**

A metal powder for powder metallurgy contains Fe as a principal component, Cr in a proportion of 10% by mass or more and 30% by mass or less, C in a proportion of 0.15% by mass or more and 1.5% by mass or less, Si in a proportion of 0.3% by mass or more and 1% by mass or less, Zr in a proportion of 0.01% by mass or more and 0.5% by mass or less, Nb in a proportion of 0.01% by mass or more and 0.5% by mass or less, and Mn and Ni in a total proportion of 0.05% by mass or more and 1.6% by mass or less. Further, the metal powder for powder metallurgy preferably has a crystal structure of martensite-based stainless steel.

## METAL POWDER FOR POWDER METALLURGY, COMPOUND, GRANULATED POWDER, AND SINTERED BODY

### BACKGROUND

[0001] 1. Technical Field

[0002] The present invention relates to a metal powder for powder metallurgy, a compound, a granulated powder, and a sintered body.

[0003] 2. Related Art

[0004] In a powder metallurgy method, a composition containing a metal powder and a binder is molded into a desired shape to obtain a molded body, and the obtained molded body is degreased and sintered, whereby a sintered body is produced. In such a process for producing a sintered body, an atomic diffusion phenomenon occurs among particles of the metal powder, and thereby the molded body is gradually densified, resulting in sintering.

[0005] For example, JP-A-2012-87416 proposes a metal powder for powder metallurgy containing Zr and Si, wherein the remainder thereof contains at least one element selected from the group consisting of Fe, Co and Ni, and inevitable elements. According to such a metal powder for powder metallurgy, the sinterability is enhanced by the action of Zr, and a sintered body having a high density can be easily produced.

[0006] Recently, the thus obtained sintered body has become widely used for a variety of machine parts, structural parts, and the like.

[0007] However, depending on the use of the sintered body, further densification is needed in some cases. In such a case, a sintered body is further subjected to an additional treatment such as a hot isostatic pressing treatment (HIP treatment) to increase the density. However, this result in a significant increase in workload, and also an increase in cost cannot be avoided.

[0008] Therefore, expectation desire for a metal powder capable of producing a sintered body having a high density without performing an additional treatment or the like has increased.

### SUMMARY

[0009] An advantage of some aspects of the invention is to provide a metal powder for powder metallurgy, a compound, and a granulated powder, each of which is capable of producing a sintered body having a high density, and a sintered body having a high density produced by using the metal powder for powder metallurgy.

[0010] A metal powder for powder metallurgy according to an aspect of the invention contains Fe as a principal component, Cr in a proportion of 10% by mass or more and 30% by mass or less, C in a proportion of 0.15% by mass or more and 1.5% by mass or less, Si in a proportion of 0.3% by mass or more and 1% by mass or less, Zr in a proportion of 0.01% by mass or more and 0.5% by mass or less, Nb in a proportion of 0.01% by mass or more and 0.5% by mass or less, and Mn and Ni in a total proportion of 0.05% by mass or more and 1.6% by mass or less.

[0011] According to this configuration, a metal powder for powder metallurgy in which the significant growth of crystal grains during sintering is inhibited due to the addition of Zr and Nb in an appropriate amount. As a result, pores are hardly generated in a sintered body and also an increase in size of

crystal grains is prevented. Thus, the metal powder is capable of producing a sintered body having a high density.

[0012] In the metal powder for powder metallurgy according to the aspect of the invention, it is preferred that the metal powder for powder metallurgy has a crystal structure of martensite-based stainless steel.

[0013] A crystal structure of martensite-based stainless steel is a body-centered cubic lattice in the form of a solid solution supersaturated with C and N, and therefore is in a slightly distorted state as compared with a general body-centered cubic lattice. Due to this, the metal powder for powder metallurgy having such a crystal structure is capable of producing a sintered body having a high hardness reflecting the distortion of this crystal structure.

[0014] In the metal powder for powder metallurgy according to the aspect of the invention, it is preferred that the ratio of the content of Zr to the content of Nb (Zr/Nb) is 0.3 or more and 3 or less.

[0015] According to this configuration, a difference in timing when crystal growth starts between a region where a Nb carbide is used as a nucleus and a region where a Zr carbide is used as a nucleus can be carefully controlled. As a result, pores remaining in the molded body can be eliminated as if they were sequentially swept from the inside, and therefore, pores generated in the sintered body can be minimized. Accordingly, by setting the Zr/Nb within the above range, a metal powder capable of producing a sintered body having a high density and excellent mechanical properties can be obtained.

[0016] In the metal powder for powder metallurgy according to the aspect of the invention, it is preferred that the sum of the content of Zr and the content of Nb is 0.05% by mass or more and 0.6% by mass or less.

[0017] According to this configuration, the densification of a sintered body to be produced becomes as desired and sufficient.

[0018] In the metal powder for powder metallurgy according to the aspect of the invention, it is preferred that when the sum of the content of Zr and the content of Nb is represented by (Zr+Nb), the ratio of (Zr+Nb) to the content of Si, (Zr+Nb)/Si, is 0.1 or more and 0.7 or less.

[0019] According to this configuration, a decrease in toughness or the like when Si is added is sufficiently compensated by the addition of Zr and Nb. As a result, a metal powder capable of producing a sintered body which has excellent mechanical properties such as toughness, although the density is high, and also has excellent corrosion resistance attributed to Si is obtained.

[0020] In the metal powder for powder metallurgy according to the aspect of the invention, it is preferred that Mn is contained in a proportion of 0.01% by mass or more and 1.25% by mass or less.

[0021] According to this configuration, a sintered body having a high density and excellent mechanical properties is obtained.

[0022] In the metal powder for powder metallurgy according to the aspect of the invention, it is preferred that Ni is contained in a proportion of 0.05% by mass or more and 0.6% by mass or less.

[0023] According to this configuration, a sintered body which maintains excellent mechanical properties over a long period of time is obtained.

[0024] In the metal powder for powder metallurgy according to the aspect of the invention, it is preferred that the metal powder has an average particle diameter of 0.5  $\mu\text{m}$  or more and 30  $\mu\text{m}$  or less.

[0025] According to this configuration, pores remaining in the sintered body are extremely reduced, and therefore, a sintered body having a particularly high density and particularly excellent mechanical properties can be produced.

[0026] A compound according to another aspect of the invention contains the metal powder for powder metallurgy according to the aspect of the invention and a binder which binds the particles of the metal powder for powder metallurgy to one another.

[0027] According to this configuration, a compound capable of producing a sintered body having a high density is obtained.

[0028] A granulated powder according to still another aspect of the invention is obtained by granulating the metal powder for powder metallurgy according to the aspect of the invention.

[0029] According to this configuration, a granulated powder capable of producing a sintered body having a high density is obtained.

[0030] A sintered body according to yet another aspect of the invention is produced by sintering a metal powder for powder metallurgy containing Fe as a principal component, Cr in a proportion of 10% by mass or more and 30% by mass or less, C in a proportion of 0.15% by mass or more and 1.5% by mass or less, Si in a proportion of 0.3% by mass or more and 1% by mass or less, Zr in a proportion of 0.01% by mass or more and 0.5% by mass or less, Nb in a proportion of 0.01% by mass or more and 0.5% by mass or less, and Mn and Ni in a total proportion of 0.05% by mass or more and 1.6% by mass or less.

[0031] According to this configuration, a sintered body having a high density is obtained.

[0032] In the sintered body according to the aspect of the invention, it is preferred that the sintered body has a relative density of 97% or more and a surface Vickers hardness of 570 or more.

[0033] According to this configuration, a sintered body has excellent mechanical properties comparable to those of ingot materials although it has a shape substantially identical to the desired shape, and therefore, a sintered body which can be applied to a variety of machine parts, structural parts, and the like is obtained almost without performing post-processing.

#### DESCRIPTION OF EXEMPLARY EMBODIMENTS

[0034] Hereinafter, a metal powder for powder metallurgy, a compound, a granulated powder, and a sintered body according to embodiments of the invention will be described in detail.

##### Metal Powder for Powder Metallurgy

[0035] First, a metal powder for powder metallurgy will be described.

[0036] In powder metallurgy, a sintered body having a desired shape can be obtained by molding a composition containing a metal powder for powder metallurgy and a binder into a desired shape, followed by degreasing and sintering. According to such a powder metallurgy technique, an advantage that a sintered body with a complicated and fine

shape can be produced in a near-net shape (close to a final shape) as compared with the other metallurgy techniques is obtained.

[0037] As the metal powder for powder metallurgy to be used in the powder metallurgy, an attempt to densify a sintered body to be produced by appropriately changing the composition thereof has been made. However, in the sintered body, pores are liable to be generated, and therefore, in order to obtain mechanical properties comparable to those of ingot materials, it was necessary to increase the density by way of an additional step.

[0038] That is, in the past, the obtained sintered body was further subjected to an additional treatment such as a hot isostatic pressing treatment (HIP treatment) to increase the density. However, such an additional treatment requires much time, labor and cost, and therefore becomes an obstacle to the expansion of the application of the sintered body.

[0039] In consideration of the above-described problems, the present inventors have made extensive studies to find conditions for obtaining a sintered body having a high density without performing an additional treatment. As a result, they found that a sintered body is densified by carefully selecting the composition of an alloy which forms a metal powder.

[0040] Specifically, the metal powder for powder metallurgy according to an embodiment of the invention is a metal powder which contains Fe as a principal component, Cr in a proportion of 10% by mass or more and 30% by mass or less, C in a proportion of 0.15% by mass or more and 1.5% by mass or less, Si in a proportion of 0.3% by mass or more and 1% by mass or less, Zr in a proportion of 0.01% by mass or more and 0.5% by mass or less, Nb in a proportion of 0.01% by mass or more and 0.5% by mass or less, and Mn and Ni in a total proportion of 0.05% by mass or more and 1.6% by mass or less. According to such a metal powder, as a result of carefully selecting the composition of an alloy, the densification during sintering can be particularly enhanced. As a result, a sintered body having a high density can be produced without performing an additional treatment.

[0041] By densifying a sintered body, a sintered body having excellent mechanical properties is obtained. Such a sintered body can be widely applied also to, for example, machine parts, structural parts, and the like, to which an external force (load) is applied.

[0042] Hereinafter, the composition of an alloy of the metal powder for powder metallurgy according to an embodiment of the invention will be described in further detail. In the following description, the "metal powder for powder metallurgy" is sometimes simply referred to as "metal powder".

[0043] Cr (chromium) is an element which imparts corrosion resistance to a sintered body to be produced. By using the metal powder containing Cr, a sintered body capable of maintaining high mechanical properties over a long period of time is obtained.

[0044] The content of Cr in the metal powder is set to 10% by mass or more and 30% by mass or less, preferably 10.5% by mass or more and 20% by mass or less, and more preferably 11% by mass or more and 18% by mass or less. If the content of Cr is less than the above lower limit, the corrosion resistance of a sintered body to be produced is insufficient depending on the overall composition. On the other hand, if the content of Cr exceeds the above upper limit, the sinterability is deteriorated depending on the overall composition so that it becomes difficult to densify the sintered body.

[0045] C (carbon) can particularly enhance the sinterability when it is used in combination with Zr and Nb, which will be described below. Specifically, each of Zr and Nb binds to C, whereby carbides such as ZrC and NbC are formed. By dispersing and depositing these carbides such as ZrC and NbC, an effect of preventing the significant growth of crystal grains is exhibited. A clear reason for obtaining such an effect is not known, but one of the reasons therefor is considered that a dispersed deposit serves as an obstacle to inhibit the significant growth of crystal grains, and therefore, a variation in size of crystal grains is prevented. Accordingly, it becomes difficult to generate pores in a sintered body, and also the increase in size of crystal grains is prevented, and thus, a sintered body having a high density and excellent mechanical properties is obtained.

[0046] The content of C in the metal powder is set to 0.15% by mass or more and 1.5% by mass or less, preferably 0.35% by mass or more and 1.15% by mass or less, and more preferably 0.4% by mass or more and 1.1% by mass or less. If the content of C is less than the above lower limit, crystal grains are liable to grow significantly depending on the overall composition so that the mechanical properties of the sintered body are insufficient. On the other hand, if the content of C exceeds the above upper limit, the amount of C is too much depending on the overall composition so that the sinterability is deteriorated instead.

[0047] Si (silicon) is an element which imparts corrosion resistance and high mechanical properties to a sintered body to be produced, and by using the metal powder containing Si, a sintered body capable of maintaining high mechanical properties over a long period of time is obtained.

[0048] The content of Si in the metal powder is set to 0.3% by mass or more and 0.9% by mass or less, preferably 0.4% by mass or more and 0.85% by mass or less, and more preferably 0.5% by mass or more and 0.8% by mass or less. If the content of Si is less than the above lower limit, the effect of the addition of Si is weakened depending on the overall composition so that the corrosion resistance and the mechanical properties of a sintered body to be produced are deteriorated. On the other hand, if the content of Si exceeds the above upper limit, the amount of Si is too much depending on the overall composition so that the corrosion resistance and the mechanical properties are deteriorated instead.

[0049] Zr (zirconium) is solid-soluted in Fe and forms a low-melting point phase. However, this low-melting point phase causes rapid atomic diffusion when sintering the metal powder. This atomic diffusion acts as a driving force, and thereby a distance between particles of the metal powder is rapidly decreased and a neck is formed between the particles. As a result, densification of a molded body proceeds, and the molded body is rapidly sintered.

[0050] On the other hand, the atomic radius of Zr is slightly larger than that of Fe. Specifically, the atomic radius of Fe is about 0.117 nm, and the atomic radius of Zr is 0.145 nm. Therefore, Zr is solid-soluted in Fe, but is not completely solid-soluted therein, and part of Zr is deposited as a Zr carbide such as ZrC. Due to this, this deposited Zr carbide inhibits the significant growth of crystal grains. As a result, as described above, it becomes difficult to generate pores in a sintered body, and also the increase in size of crystal grains is prevented, and thus, a sintered body having a high density and excellent mechanical properties is obtained.

[0051] In addition, although a detailed description will be given later, the deposited Zr carbide promotes the accumula-

tion of a silicon oxide in a crystal grain boundary, and as a result, the sintering is promoted and the density is increased while preventing the increase in size of crystal grains.

[0052] Further, Zr is a ferrite forming element, and therefore deposits a body-centered cubic lattice phase. This body-centered cubic lattice phase has more excellent sinterability than the other crystal lattice phases, and therefore contributes to the densification of a sintered body.

[0053] In addition, Zr acts as a deoxidizing agent which removes oxygen contained as an oxide in the metal powder. Therefore, Zr can decrease the content of oxygen which is one of the causes of deterioration of sinterability, and thus, the density of the sintered body can be further increased.

[0054] The content of Zr in the metal powder is set to 0.01% by mass or more and 0.5% by mass or less, preferably 0.03% by mass or more and 0.2% by mass or less, and more preferably 0.05% by mass or more and 0.1% by mass or less. If the content of Zr is less than the above lower limit, the effect of the addition of Zr is weakened depending on the overall composition so that the densification of a sintered body to be produced is insufficient. On the other hand, if the content of Zr exceeds the above upper limit, the amount of Zr is too much depending on the overall composition so that the densification is impeded instead.

[0055] Also the atomic radius of Nb (niobium) is slightly larger than that of Fe, but slightly smaller than that of Zr. Specifically, the atomic radius of Fe is about 0.117 nm, and the atomic radius of Nb is about 0.134 nm. Therefore, part of the Nb is deposited as a Nb carbide such as NbC. Therefore, it is considered that a Zr carbide and a Nb carbide are deposited during sintering, respectively, and these deposits inhibit the significant growth of crystal grains, and also promote the accumulation of a silicon oxide in a crystal grain boundary.

[0056] On the other hand, with respect to such deposition of a Zr carbide and a Nb carbide, the deposition of a Zr carbide starts at a lower temperature range than the deposition of a Nb carbide. The reason therefor is not clear, but it is considered that a difference in atomic radius between Zr and Nb is involved. Then, it is presumed that due to a difference in temperature range at which carbides are deposited as described above, when the metal powder is sintered, the timing when the effect of the deposition of a Nb carbide is exhibited is different from the timing when the effect of the deposition of a Zr carbide is exhibited. It is considered that due to the difference in timing when a carbide is deposited in this manner, the generation of pores is inhibited, and thus, a dense sintered body is obtained. That is, it is considered that by the existence of both Nb carbide and Zr carbide, the increase in size of crystal grains can be inhibited while increasing the density of the sintered body.

[0057] The content of Nb in the metal powder is set to 0.01% by mass or more and 0.5% by mass or less, preferably 0.03% by mass or more and 0.2% by mass or less, and more preferably 0.05% by mass or more and 0.1% by mass or less. If the content of Nb is less than the above lower limit, the effect of the addition of Nb is weakened depending on the overall composition so that the densification of a sintered body to be produced is insufficient. On the other hand, if the content of Nb exceeds the above upper limit, the amount of Nb is too much depending on the overall composition so that the densification is impeded instead.

[0058] When the ratio of the content of Zr to the content of Nb is represented by Zr/Nb, Zr/Nb is preferably 0.3 or more and 3 or less, and more preferably 0.5 or more and 2 or less.

By setting the Zr/Nb within the above range, a difference in timing between when the Nb carbide is deposited and when the Zr carbide is deposited can be carefully controlled. Due to this, pores remaining in the molded body can be eliminated as if they were sequentially swept from the inside, and therefore, pores generated in the sintered body can be minimized. Accordingly, by setting the Zr/Nb within the above range, a metal powder capable of producing a sintered body having a high density and excellent mechanical properties can be obtained.

[0059] Further, the content of Zr and the content of Nb are as described above, respectively, however, the sum of these contents is preferably 0.05% by mass or more and 0.6% by mass or less, more preferably 0.10% by mass or more and 0.48% by mass or less, and further more preferably 0.12% by mass or more and 0.24% by mass or less. By setting the sum of the content of Zr and the content of Nb within the above range, the densification of a sintered body to be produced becomes as desired and sufficient.

[0060] When the ratio of the sum of the content of Zr and the content of Nb to the content of Si is represented by  $(\text{Zr}+\text{Nb})/\text{Si}$ ,  $(\text{Zr}+\text{Nb})/\text{Si}$  is preferably 0.1 or more and 0.7 or less, more preferably 0.15 or more and 0.6 or less, and further more preferably 0.17 or more and 0.5 or less. By setting the  $(\text{Zr}+\text{Nb})/\text{Si}$  within the above range, a decrease in toughness or the like when Si is added is sufficiently compensated by the addition of Zr and Nb. As a result, a metal powder capable of producing a sintered body which has excellent mechanical properties such as toughness, although the density is high, and also has excellent corrosion resistance attributed to Si is obtained.

[0061] Further, it is considered that by the addition of Zr and Nb in an appropriate amount, the Zr carbide as described above and a Zr oxide, and the Nb carbide as described above and a Nb oxide (hereinafter these are collectively referred to as "Zr carbide and others") act as "nuclei", and therefore, a silicon oxide accumulates in a crystal grain boundary in the sintered body. By the accumulation of a silicon oxide in a crystal grain boundary, the concentration of oxides in the crystal is decreased, and therefore, sintering is promoted. As a result, it is considered that the densification of the sintered body is further promoted.

[0062] The deposited silicon oxide is liable to move to the triple point of a crystal grain boundary during the accumulation, and therefore, the crystal growth is inhibited at the point (a flux pinning effect). As a result, the significant growth of crystal grains is prevented, and thus, a sintered body having finer crystals is obtained. Such a sintered body has particularly high mechanical properties.

[0063] The accumulated silicon oxide is easily located at the triple point of a crystal grain boundary as described above, and therefore tends to be shaped into a particle. Therefore, in the sintered body, a first region which is in the form of such a particle and has a relatively high silicon oxide content and a second region which has a relatively low silicon oxide content than the first region are formed. By the existence of the first region, the concentration of oxides inside the crystal is decreased, and the significant growth of crystal grains is inhibited as described above.

[0064] When a qualitative and quantitative analysis is performed for the first region and the second region using an electron beam microanalyzer (EPMA), the first region contains O (oxygen) as a principal element, and the second region contains Fe as a principal element. As described above, the

first region mainly exists in a crystal grain boundary, and the second region mainly exists inside the crystal. Therefore, in the first region, when the sum of the contents of the two elements, O and Si, and the content of Fe are compared, the sum of the contents of the two components is larger than the content of Fe. On the other hand, in the second region, the sum of the contents of the two elements, O and Si, is much smaller than the content of Fe. Based on these analysis results, it is found that Si and O accumulate in the first region. Specifically, it is preferred that in the first region, the sum of the content of Si and the content of O is 1.5 times or more large than the content of Fe. Further, it is preferred that the content of Si in the first region is 3 times or more large than the content of Si in the second region.

[0065] Further, at least either of the content of Zr and the content of Nb satisfies the following relational formula: (the content in the first region) > (the content in the second region), which may vary depending on the compositional ratio. This indicates that in the first region, the above-described Zr carbide and others act as nuclei when a silicon oxide accumulates. Specifically, the content of Zr in the first region is preferably 3 times or more large than the content of Zr in the second region.

[0066] The accumulation of a silicon oxide as described above is considered to be one of the causes for the densification of a sintered body. Therefore, it is considered that even if a sintered body is densified according to an embodiment of the invention, a silicon oxide may not accumulate depending on the compositional ratio.

[0067] The diameter of the first region in the form of a particle is set to about 0.05  $\mu\text{m}$  or more and 15  $\mu\text{m}$  or less, and preferably about 0.1  $\mu\text{m}$  or more and 10  $\mu\text{m}$  or less, which varies depending on the content of Si in the entire sintered body. According to this, the densification of the sintered body can be sufficiently promoted while preventing the decrease in mechanical properties of the sintered body accompanying the accumulation of a silicon oxide.

[0068] The diameter of the first region can be obtained as the average of the diameter of a circle having the same area (circle equivalent diameter) as that of the first region determined by the gray-scale in an electron micrograph of the cross section of the sintered body. When the average is obtained, the measured values of 10 or more regions are used.

[0069] Further, when the ratio of the sum of the content of Zr and the content of Nb to the content of C is represented by  $(\text{Zr}+\text{Nb})/\text{C}$ ,  $(\text{Zr}+\text{Nb})/\text{C}$  is preferably 0.05 or more and 0.7 or less, more preferably 0.1 or more and 0.5 or less, and further more preferably 0.13 or more and 0.35 or less. By setting the  $(\text{Zr}+\text{Nb})/\text{C}$  within the above range, an increase in hardness and a decrease in toughness brought about by the addition of C, and an increase in density brought about by the addition of Zr and Nb can be achieved. As a result, a metal powder capable of producing a sintered body which has excellent mechanical properties such as tensile strength and toughness is obtained.

[0070] Mn is an element which imparts corrosion resistance and high mechanical properties to a sintered body to be produced in the same manner as Si.

[0071] The content of Mn in the metal powder is preferably 0.01% by mass or more and 1.25% by mass or less, more preferably 0.03% by mass or more and 0.3% by mass or less, and further more preferably 0.05% by mass or more and 0.2% by mass or less. By setting the content of Mn within the above

range, a sintered body having a high density and excellent mechanical properties is obtained.

[0072] If the content of Mn is less than the above lower limit, the corrosion resistance and the mechanical properties of a sintered body to be produced may not be sufficiently enhanced depending on the overall composition. On the other hand, if the content of Mn exceeds the above upper limit, the corrosion resistance and the mechanical properties may be deteriorated instead.

[0073] Ni is an element which imparts corrosion resistance and heat resistance to a sintered body to be produced as expected.

[0074] The content of Ni in the metal powder is preferably 0.05% by mass or more and 0.6% by mass or less, more preferably 0.06% by mass or more and 0.4% by mass or less, and further more preferably 0.07% by mass or more and 0.25% by mass or less. By setting the content of Ni within the above range, a sintered body which maintains excellent mechanical properties over a long period of time is obtained.

[0075] If the content of Ni is less than the above lower limit, the corrosion resistance and the heat resistance of a sintered body to be produced may not be sufficiently enhanced depending on the overall composition. On the other hand, if the content of Ni exceeds the above upper limit, the corrosion resistance and the heat resistance may be deteriorated instead.

[0076] Further, Mn and Ni are contained in a total proportion of 0.05% by mass or more and 1.6% by mass or less. According to this, the mechanical properties of the sintered body can be particularly enhanced. The sum of the content of Mn and the content of Ni is preferably 0.08% by mass or more and 1.3% by mass or less, and more preferably 0.1% by mass or more and 1% by mass or less. Further, the total content of Mn and Ni may be within the above range, and the content of either Mn or Ni may be 0.

[0077] The metal powder for powder metallurgy according to an embodiment of the invention may contain at least one element selected from Mo, Pb, S, and Al as desired other than the above-described elements. These elements may be inevitably contained in some cases.

[0078] Mo is an element which enhances the corrosion resistance of a sintered body to be produced.

[0079] The content of Mo in the metal powder is preferably 0.2% by mass or more and 0.8% by mass or less, and more preferably 0.3% by mass or more and 0.6% by mass or less. By setting the content of Mo within the above range, the corrosion resistance of a sintered body to be produced can be further enhanced.

[0080] Pb is an element which enhances the machinability of a sintered body to be produced.

[0081] The content of Pb in the metal powder is preferably 0.03% by mass or more and 0.5% by mass or less, and more preferably 0.05% by mass or more and 0.3% by mass or less. By setting the content of Pb within the above range, the machinability of a sintered body to be produced can be further enhanced.

[0082] S is an element which enhances the machinability of a sintered body to be produced.

[0083] The content of S in the metal powder is not particularly limited, but is preferably 0.5% by mass or less, and more preferably 0.01% by mass or more and 0.3% by mass or less. By setting the content of S within the above range, the machinability of a sintered body to be produced can be further enhanced without causing a large decrease in density of the sintered body to be produced.

[0084] Al is an element which enhances the oxidation resistance of a sintered body to be produced.

[0085] The content of Al in the metal powder is not particularly limited, but is preferably 0.5% by mass or less, and more preferably 0.05% by mass or more and 0.3% by mass or less. By setting the content of Al within the above range, the oxidation resistance of a sintered body to be produced can be further enhanced without causing a large decrease in density of the sintered body to be produced.

[0086] In addition to the elements described above, the metal powder for powder metallurgy according to an embodiment of the invention may further contain impurities. Examples of the impurities include all elements other than the above-described Fe, Cr, C, Si, Zr, Nb, Mn, Ni, Mo, Pb, S, and Al, and specific examples thereof include Li, Be, B, N, Na, Mg, P, K, Ca, Sc, Ti, V, Co, Zn, Ga, Ge, Y, Pd, Ag, In, Sn, Sb, Hf, Ta, W, Os, Ir, Pt, Au, and Bi. The incorporation amount of these impurity elements is preferably set such that the content of each of the impurity elements is less than the content of each of the following elements: Fe, Cr, C, Si, Zr, and Nb. Further, the incorporation amount of these impurity elements is preferably set such that the content of each of the impurity elements is less than 0.03% by mass, and more preferably less than 0.02% by mass. Further, the total content of these impurity elements is set to preferably less than 0.3% by mass, and more preferably less than 0.2% by mass. These elements do not inhibit the above-described effects as long as the content thereof is within the above range, and therefore may be intentionally added to the metal powder.

[0087] Meanwhile, O (oxygen) may also be intentionally added to or inevitably mixed in the metal powder, however, the amount thereof is preferably about 0.8% by mass or less, and more preferably about 0.5% by mass or less. By controlling the amount of oxygen in the metal powder within the above range, the sinterability is enhanced, and thus, a sintered body having a higher density and more excellent mechanical properties is obtained. Incidentally, the lower limit thereof is not particularly set, but is preferably 0.03% by mass or more from the viewpoint of easy mass production or the like.

[0088] It is preferred that the metal powder for powder metallurgy according to an embodiment of the invention substantially contains no Cu. A clear reason therefor is not known, however, this is likely due to the finding that by the incorporation of Cu, depending on the overall composition, the effects brought about by Zr and Nb as described above may be weakened. Specifically, the content of Cu is set to preferably less than 0.02% by mass or less, and more preferably less than 0.01% by mass.

[0089] Fe is a component (principal component) whose content is the largest in the metal powder for powder metallurgy according to an embodiment of the invention, and has a great effect on the properties of the sintered body. The content of Fe is 50% by mass or more.

[0090] The compositional ratio of the metal powder for powder metallurgy can be determined by, for example, atomic absorption spectrometry specified in JIS G 1257, ICP optical emission spectroscopy specified in JIS G 1258, spark optical emission spectroscopy specified in JIS G 1253, X-ray fluorescence spectroscopy specified in JIS G 1256, gravimetry, titrimetry, and absorption spectroscopy specified in JIS G 1211 to G 1237, or the like. Specifically, for example, a solid optical emission spectrometer (spark optical emission spectrometer, model: SPECTROLAB, type: LAVMBO8A) manufactured by SPECTRO Analytical Instruments GmbH

or an ICP device (model: CIROS-120) manufactured by Rigaku Corporation can be used.

[0091] Further, when C (carbon) and S (sulfur) are determined, particularly, an infrared absorption method after combustion in a current of oxygen (after combustion in a high-frequency induction heating furnace) specified in JIS G 1211 is also used. Specifically, a carbon-sulfur analyzer, CS-200 manufactured by LECO Corporation can be used.

[0092] Further, when N (nitrogen) and O (oxygen) are determined, particularly, a method for determination of nitrogen content in iron and steel specified in JIS G 1228 and a method for determination of oxygen content in metallic materials specified in JIS Z 2613 are also used. Specifically, an oxygen-nitrogen analyzer, TC-300/EF-300 manufactured by LECO Corporation can be used.

[0093] The metal powder for powder metallurgy according to an embodiment of the invention preferably has a crystal structure of martensite-based stainless steel. The crystal structure of martensite-based stainless steel is a body-centered cubic lattice in the form of a solid solution supersaturated with C and N, and therefore is in a slightly distorted state as compared with a general body-centered cubic lattice. Due to this, the metal powder for powder metallurgy having such a crystal structure is capable of producing a sintered body having a high hardness reflecting the distortion of this crystal structure.

[0094] It can be determined whether or not the metal powder for powder metallurgy has a crystal structure of martensite-based stainless steel by, for example, X-ray diffractometry.

[0095] The average particle diameter of the metal powder for powder metallurgy according to an embodiment of the invention is preferably 0.5  $\mu\text{m}$  or more and 30  $\mu\text{m}$  or less, more preferably 1  $\mu\text{m}$  or more and 20  $\mu\text{m}$  or less, and further more preferably 2  $\mu\text{m}$  or more and 10  $\mu\text{m}$  or less. By using the metal powder for powder metallurgy having such a particle diameter, pores remaining in the sintered body are extremely reduced, and therefore, a sintered body having a particularly high density and particularly excellent mechanical properties can be produced.

[0096] The average particle diameter is obtained as a particle diameter when the cumulative amount obtained by cumulating the percentages of the particles from the smaller diameter side reaches 50% in a cumulative particle size distribution on a mass basis obtained by a laser diffractometry.

[0097] If the average particle diameter of the metal powder for powder metallurgy is less than the above lower limit, the moldability is deteriorated in the case where the shape is difficult to mold, and therefore, the sintered density may be decreased. On the other hand, if the average particle diameter of the metal powder exceeds the above upper limit, the size of a space among the particles is increased during molding, and therefore, the sintered density may be decreased in the same manner.

[0098] The particle size distribution of the metal powder for powder metallurgy is preferably as narrow as possible. Specifically, when the average particle diameter of the metal powder for powder metallurgy is within the above range, the maximum particle diameter of the metal powder is preferably 200  $\mu\text{m}$  or less, and more preferably 150  $\mu\text{m}$  or less. By controlling the maximum particle diameter of the metal powder for powder metallurgy within the above range, the particle size distribution of the metal powder for powder metallurgy

can be made narrower, and thus, the density of the sintered body can be further increased.

[0099] Here, the "maximum particle diameter" refers to a particle diameter when the cumulative amount obtained by cumulating the percentages of the particles from the smaller diameter side reaches 99.9% in a cumulative particle size distribution on a mass basis obtained by a laser diffractometry.

[0100] The average of the aspect ratio of the particle of the metal powder for powder metallurgy defined by S/L wherein S ( $\mu\text{m}$ ) represents the minor axis of each particle and L ( $\mu\text{m}$ ) represents the major axis thereof is preferably about 0.4 or more and 1 or less, and more preferably about 0.7 or more and 1 or less. The metal powder for powder metallurgy having an aspect ratio within this range has a shape relatively close to a spherical shape, and therefore, the packing factor when the metal powder is molded is increased. As a result, the density of the sintered body can be further increased.

[0101] Here, the "major axis" is the maximum length in the projected image of the particle, and the "minor axis" is the maximum length in the direction perpendicular to the major axis. Incidentally, the average of the aspect ratio is obtained as the average of the measured aspect ratios of 100 or more particles of the metal powder.

[0102] The tap density of the metal powder for powder metallurgy according to an embodiment of the invention is preferably 3.5  $\text{g}/\text{cm}^3$  or more, and more preferably 4  $\text{g}/\text{cm}^3$  or more. According to the metal powder for powder metallurgy having such a high tap density, when a molded body is obtained, the packing density among the particles is particularly increased. Therefore, a particularly dense sintered body can be obtained in the end.

[0103] The specific surface area of the metal powder for powder metallurgy according to an embodiment of the invention is not particularly limited, but is preferably 0.1  $\text{m}^2/\text{g}$  or more, and more preferably 0.2  $\text{m}^2/\text{g}$  or more. According to the metal powder for powder metallurgy having such a large specific surface area, a surface activity (surface energy) is increased so that it is possible to easily sinter the metal powder by applying a relatively small energy. Therefore, when a molded body is sintered, a difference in sintering rate hardly occurs between the inner side and the outer side of the molded body, and thus, the decrease in sintered density due to the pores remaining inside the molded body can be prevented.

#### Method for Producing Sintered Body

[0104] Next, a method for producing a sintered body using such a metal powder for powder metallurgy according to an embodiment of the invention will be described.

[0105] The method for producing a sintered body includes (A) a composition preparation step in which a composition for producing a sintered body is prepared, (B) a molding step in which a molded body is produced, (C) a degreasing step in which a degreasing treatment is performed, and (D) a firing step in which firing is performed. Hereinafter, the respective steps will be described sequentially.

##### (A) Composition Preparation Step

[0106] First, the metal powder for powder metallurgy according to an embodiment of the invention and a binder are prepared, and these materials are kneaded using a kneader, whereby a kneaded material (composition) is obtained.

[0107] In this kneaded material (an embodiment of the compound according to the invention), the metal powder for powder metallurgy is uniformly dispersed.

[0108] The metal powder for powder metallurgy according to an embodiment of the invention is produced by, for example, any of a variety of powdering methods such as an atomization method (such as a water atomization method, a gas atomization method, or a spinning water atomization method), a reducing method, a carbonyl method, and a pulverization method.

[0109] Among these, the metal powder for powder metallurgy according to an embodiment of the invention is preferably a metal powder produced by an atomization method, and more preferably a metal powder produced by a water atomization method or a spinning water atomization method. The atomization method is a method in which a molten metal (a metal melt) is caused to collide with a fluid (a liquid or a gas) sprayed at a high speed to atomize the metal melt, followed by cooling, whereby a metal powder is produced. By producing the metal powder for powder metallurgy through such an atomization method, an extremely fine powder can be efficiently produced. Further, the shape of the particle of the obtained powder is closer to a spherical shape by the action of surface tension. Due to this, when the metal powder is molded, a molded body having a high packing factor is obtained. Accordingly, a powder capable of producing a sintered body having a high density can be obtained.

[0110] In the case where a water atomization method is used as the atomization method, the pressure of water (hereinafter referred to as "atomization water") to be sprayed to the molten metal is not particularly limited, but is set to preferably about 75 MPa or more and 120 MPa or less (750 kgf/cm<sup>2</sup> or more and 1200 kgf/cm<sup>2</sup> or less), and more preferably about 90 MPa or more and 120 MPa or less (900 kgf/cm<sup>2</sup> or more and 1200 kgf/cm<sup>2</sup> or less).

[0111] The temperature of the atomization water is also not particularly limited, but is preferably set to about 1° C. or higher and 20° C. or lower.

[0112] The atomization water is often sprayed in a cone shape such that it has a vertex on the fall path of the metal melt and the outer diameter gradually decreases downward. In this case, the vertex angle  $\theta$  of the cone formed by the atomization water is preferably about 10° or more and 40° or less, and more preferably about 15° or more and 35° or less. According to this, a metal powder for powder metallurgy having a composition as described above can be reliably produced.

[0113] Further, by using a water atomization method (particularly, a spinning water atomization method), the metal melt can be particularly quickly cooled. Due to this, a powder having high quality is obtained over a wide alloy composition range.

[0114] The cooling rate when cooling the metal melt in the atomization method is preferably  $1 \times 10^4$  °C./s or more, and more preferably  $1 \times 10^5$  °C./s or more. By the quick cooling in this manner, for example, in the case of a metal powder for powder metallurgy having a crystal structure of martensite-based stainless steel, the ratio of residual austenite can be reduced, and therefore, a powder with a low variation in properties is obtained. As a result, a sintered body having high quality can be obtained.

[0115] The thus obtained metal powder for powder metallurgy may be appropriately classified. Examples of the classification method include dry process classification such as

sieving classification, inertial classification, and centrifugal classification, and wet process classification such as sedimentation classification.

[0116] Examples of the binder include polyolefins such as polyethylene, polypropylene, and ethylene-vinyl acetate copolymers, acrylic resins such as polymethyl methacrylate and polybutyl methacrylate, styrenic resins such as polystyrene, polyesters such as polyvinyl chloride, polyvinylidene chloride, polyamide, polyethylene terephthalate, and polybutylene terephthalate, various resins such as polyether, polyvinyl alcohol, polyvinyl pyrrolidone, and copolymers thereof, and various organic binders such as various waxes, paraffins, higher fatty acids (such as stearic acid), higher alcohols, higher fatty acid esters, and higher fatty acid amides. These can be used alone or by mixing two or more types thereof.

[0117] Among these, as the binder, a binder containing a polyolefin as a principal component is preferred. The polyolefin has a relatively high decomposability by a reducing gas. Therefore, in the case where a polyolefin is used as a principal component of the binder, the molded body can be reliably degreased in a shorter time.

[0118] The content of the binder is preferably about 2% by mass or more and 20% by mass or less, and more preferably about 5% by mass or more and 10% by mass or less with respect to the total amount of the kneaded material. By setting the content of the binder within the above range, a molded body can be formed with good moldability, and also the density is increased, whereby the stability of the shape of the molded body and the like can be particularly enhanced. Further, according to this, a difference in size between the molded body and the degreased body, that is, a shrinkage ratio is controlled, whereby a decrease in the dimensional accuracy of the finally obtained sintered body can be prevented. That is, a sintered body having a high density and high dimensional accuracy can be obtained.

[0119] In the kneaded material, a plasticizer may be added as desired. Examples of the plasticizer include phthalate esters (such as DOP, DEP, and DBP), adipate esters, trimellitate esters, and sebacate esters. These can be used alone or by mixing two or more types thereof.

[0120] Further, in the kneaded material, other than the metal powder for powder metallurgy, the binder, and the plasticizer, for example, any of a variety of additives such as a lubricant, an antioxidant, a degreasing accelerator, and a surfactant may be added as desired.

[0121] The kneading conditions vary depending on the respective conditions such as the metal composition or the particle diameter of the metal powder for powder metallurgy to be used, the composition of the binder, and the blending amount thereof. However, as one example, the following conditions can be exemplified: the kneading temperature: about 50° C. or higher and 200° C. or lower, and the kneading time: about 15 minutes or more and 210 minutes or less.

[0122] Further, the kneaded material is formed into a pellet (small particle) as desired. The particle diameter of the pellet is set to, for example, about 1 mm or more and 15 mm or less.

[0123] Incidentally, depending on the molding method described below, in place of the kneaded material, a granulated powder may be produced.

[0124] The granulated powder is configured such that a plurality of metal particles are bound to one another with the binder by subjecting the metal powder to a granulation treatment.

[0125] Examples of the binder to be used for producing the granulated powder include polyolefins such as polyethylene, polypropylene, and ethylene-vinyl acetate copolymers, acrylic resins such as polymethyl methacrylate and polybutyl methacrylate, styrenic resins such as polystyrene, polyesters such as polyvinyl chloride, polyvinylidene chloride, polyamide, polyethylene terephthalate, and polybutylene terephthalate, various resins such as polyether, polyvinyl alcohol, polyvinyl pyrrolidone, and copolymers thereof, and various organic binders such as various waxes, paraffins, higher fatty acids (such as stearic acid), higher alcohols, higher fatty acid esters, and higher fatty acid amides. These can be used alone or by mixing two or more types thereof.

[0126] Among these, as the binder, a binder containing a polyvinyl alcohol or polyvinyl pyrrolidone is preferred. These binder components have a high binding ability, and therefore can efficiently form the granulated powder even in a relatively small amount. Further, the heat decomposability thereof is high, and therefore, the binder can be reliably decomposed and removed in a short time during degreasing and firing.

[0127] The content of the binder is preferably about 0.2% by mass or more and 10% by mass or less, more preferably about 0.3% by mass or more and 5% by mass or less, and further more preferably about 0.3% by mass or more and 2% by mass or less with respect to the total amount of the granulated powder. By setting the content of the binder within the above range, the granulated powder can be efficiently formed while reliably preventing significantly large particles from being formed or the metal particles which are not granulated from remaining. Further, since the moldability is improved, the stability of the shape of the molded body and the like can be particularly enhanced. Further, by setting the content of the binder within the above range, a difference in size between the molded body and the degreased body, that is, a shrinkage ratio is controlled, whereby a decrease in the dimensional accuracy of the finally obtained sintered body can be prevented.

[0128] Further, in the granulated powder, any of a variety of additives such as a plasticizer, a lubricant, an antioxidant, a degreasing accelerator, and a surfactant may be added as desired.

[0129] Examples of the granulation treatment include a spray drying method, a tumbling granulation method, a fluidized bed granulation method, and a tumbling fluidized bed granulation method.

[0130] In the granulation treatment, an appropriate solvent which dissolves the binder is used. Examples of the solvent include inorganic solvents such as water and carbon tetrachloride, and organic solvents such as ketone-based solvents, alcohol-based solvents, ether-based solvents, cellosolve-based solvents, aliphatic hydrocarbon-based solvents, aromatic hydrocarbon-based solvents, aromatic heterocyclic compound-based solvents, amide-based solvents, halogen compound-based solvents, ester-based solvents, amine-based solvents, nitrile-based solvents, nitro-based solvents, and aldehyde-based solvents, and one type or a mixture of two or more types selected from these solvents is used.

[0131] The average particle diameter of the granulated powder is not particularly limited, and is preferably about 10  $\mu\text{m}$  or more and 200  $\mu\text{m}$  or less, more preferably about 20  $\mu\text{m}$  or more and 100  $\mu\text{m}$  or less, and further more preferably about 25  $\mu\text{m}$  or more and 60  $\mu\text{m}$  or less. The granulated powder

having such a particle diameter has favorable fluidity, and can more faithfully reflect the shape of a molding die.

#### (B) Molding Step

[0132] Subsequently, the kneaded material or the granulated powder is molded, whereby a molded body having the same shape as that of a desired sintered body is produced.

[0133] The method for producing a molded body (molding method) is not particularly limited, and for example, any of a variety of molding methods such as a compact molding (compression molding) method, a metal powder injection molding (MIM: Metal Injection Molding) method, and an extrusion molding method can be used.

[0134] The molding conditions in the case of a compact molding method among these methods are preferably such that the molding pressure is about 200 MPa or more and 1000 MPa or less (2 t/cm<sup>2</sup> or more and 10 t/cm<sup>2</sup> or less), which vary depending on the respective conditions such as the composition and the particle diameter of the metal powder for powder metallurgy to be used, the composition of the binder, and the blending amount thereof.

[0135] The molding conditions in the case of a metal powder injection molding method are preferably such that the material temperature is about 80° C. or higher and 210° C. or lower, and the injection pressure is about 50 MPa or more and 500 MPa or less (0.5 t/cm<sup>2</sup> or more and 5 t/cm<sup>2</sup> or less), which vary depending on the respective conditions.

[0136] The molding conditions in the case of an extrusion molding method are preferably such that the material temperature is preferably about 80° C. or higher and 210° C. or lower, and the extrusion pressure is preferably about 50 MPa or more and 500 MPa or less (0.5 t/cm<sup>2</sup> or more and 5 t/cm<sup>2</sup> or less), which vary depending on the respective conditions.

[0137] The thus obtained molded body is in a state where the binder is uniformly distributed in the spaces among the particles of the metal powder.

[0138] The shape and size of the molded body to be produced are determined in anticipation of shrinkage of the molded body in the subsequent degreasing step and firing step.

#### (C) Degreasing Step

[0139] Subsequently, the thus obtained molded body is subjected to a degreasing treatment (binder removal treatment), whereby a degreased body is obtained.

[0140] Specifically, the degreasing treatment is performed as follows: the binder is decomposed by heating the molded body, whereby the binder is removed from the molded body.

[0141] Examples of the degreasing treatment include a method of heating the molded body and a method of exposing the molded body to a gas capable of decomposing the binder.

[0142] In the case of using the method of heating the molded body, the conditions for heating the molded body are preferably such that the temperature is about 100° C. or higher and 750° C. or lower, and the time is about 0.1 hours or more and 20 hours or less, and more preferably such that the temperature is about 150° C. or higher and 600° C. or lower, and the time is about 0.5 hours or more and 15 hours or less, which slightly vary depending on the composition and the blending amount of the binder. According to this, the degreasing of the molded body can be necessarily and sufficiently performed without sintering the molded body. As a result, it is

possible to reliably prevent a large amount of the binder component from remaining inside the degreased body.

[0143] The atmosphere when the molded body is heated is not particularly limited, and an atmosphere of a reducing gas such as hydrogen, an atmosphere of an inert gas such as nitrogen or argon, an atmosphere of an oxidative gas such as air, a reduced pressure atmosphere obtained by reducing the pressure of such an atmosphere, or the like can be used.

[0144] Examples of the gas capable of decomposing the binder include ozone gas.

[0145] Incidentally, by dividing this degreasing step into a plurality of steps in which the degreasing conditions are different, and performing the plurality of steps, the binder in the molded body can be more rapidly decomposed and removed so that the binder does not remain in the molded body.

[0146] Further, if desired, the degreased body may be subjected to a machining process such as grinding, polishing, or cutting. The degreased body has a relatively low hardness and relatively high plasticity, and therefore, the machining process can be easily performed while preventing the degreased body from losing its shape. According to such a machining process, a sintered body having high dimensional accuracy in the end can be easily obtained.

#### (D) Firing Step

[0147] The degreased body obtained in the above step (C) is fired in a firing furnace, whereby a sintered body is obtained.

[0148] By this sintering, in the metal powder for powder metallurgy, diffusion occurs at the boundary surface between the particles, resulting in sintering. At this time, by the mechanism as described above, the degreased body is rapidly sintered. As a result, a sintered body which is entirely dense and has a high density is obtained.

[0149] The firing temperature varies depending on the composition, the particle diameter, and the like of the metal powder for powder metallurgy used in the production of the molded body and the degreased body, but is set to, for example, about 980°C. or higher and 1330°C. or lower, and more preferably set to about 1050°C. or higher and 1260°C. or lower.

[0150] Further, the firing time is set to 0.2 hours or more and 7 hours or less, but is preferably set to about 1 hour or more and 6 hours or less.

[0151] In the firing step, the firing temperature or the below-described firing atmosphere may be changed during the step.

[0152] By setting the firing conditions within such a range, it is possible to sufficiently sinter the entire degreased body while preventing the sintering from proceeding excessively to cause oversintering and an increase in size of the crystal structure. As a result, a sintered body having a high density and particularly excellent mechanical properties can be obtained.

[0153] Further, since the firing temperature is a relatively low temperature, it is easy to control the heating temperature in the firing furnace to be constant, and therefore, it is also easy to make the temperature of the degreased body constant. As a result, a more homogeneous sintered body can be obtained.

[0154] Further, since the firing temperature as described above can be sufficiently realized using a general firing furnace, and therefore, an inexpensive firing furnace can be used, and also the running cost can be suppressed. In other words, in the case where the temperature exceeds the firing tempera-

ture, it is necessary to employ an expensive firing furnace using a special heat resistant material, and also the running cost may be increased.

[0155] The atmosphere when firing is not particularly limited, however, in consideration of prevention of significant oxidation of the metal powder, an atmosphere of a reducing gas such as hydrogen, an atmosphere of an inert gas such as argon, a reduced pressure atmosphere obtained by reducing the pressure of such an atmosphere, or the like is preferably used.

[0156] The thus obtained sintered body has a high density and excellent mechanical properties. That is, a sintered body produced by molding a composition containing the metal powder for powder metallurgy according to an embodiment of the invention and a binder, followed by degreasing and sintering has a higher relative density than a sintered body obtained by sintering a metal powder in the related art. Therefore, according to an embodiment of the invention, a sintered body having a high density which could not be obtained unless an additional treatment such as an HIP treatment is performed can be realized without performing an additional treatment.

[0157] Specifically, according to an embodiment of the invention, for example, the relative density can be expected to be increased by 2% or more as compared with the related art, which slightly varies depending on the composition of the metal powder for powder metallurgy.

[0158] As a result, the relative density of the obtained sintered body can be expected to be, for example, 97% or more (preferably 98% or more, and more preferably 98.5% or more). The sintered body having a relative density within such a range has excellent mechanical properties comparable to those of ingot materials although it has a shape substantially identical to a desired shape by using a powder metallurgy technique, and therefore, the sintered body can be applied to a variety of machine parts, structural parts, and the like almost without performing post-processing.

[0159] Further, the tensile strength and the 0.2% proof stress of the sintered body produced by molding a composition containing the metal powder for powder metallurgy according to an embodiment of the invention and a binder, followed by degreasing and sintering are higher than those of a sintered body obtained by performing sintering using a metal powder in the related art in the same manner. It is considered that this is because by carefully selecting the composition of an alloy, the sinterability of the metal powder is enhanced, and thus, the mechanical properties are enhanced.

[0160] Further, the sintered body produced as described above has a high surface hardness. Specifically, for example, the surface Vickers hardness of the sintered body is expected to be 570 or more and 1200 or less, and preferably 600 or more and 1000 or less, which slightly varies depending on the composition of the metal powder for powder metallurgy. The sintered body having such a hardness has particularly high durability.

[0161] Incidentally, the sintered body has a sufficiently high density and mechanical properties even without performing an additional treatment, however, in order to further increase the density and enhance the mechanical properties, a variety of additional treatments may be performed.

[0162] As the additional treatment, for example, an additional treatment of increasing the density such as the HIP treatment described above may be performed, and also a

variety of quenching treatments, a variety of sub-zero treatments, a variety of tempering treatments, and the like may be performed. These additional treatments may be performed alone or two or more treatments thereof may be performed in combination.

[0163] Among these treatments, in the quenching treatment, after the sintered body is heated to about 980° C. or higher and 1200° C. or lower for about 0.2 hours or more and 3 hours or less, a rapid cooling treatment is performed. By doing this, the crystal structure of austenite can be transformed into the crystal structure of martensite, which varies depending on the composition of the metal powder for powder metallurgy. Accordingly, this treatment is preferably used, for example, when a sintered body containing the crystal structure of martensite-based stainless steel is produced.

[0164] For the rapid cooling in the quenching treatment, water cooling, oil cooling, or the like is used.

[0165] Further, the sub-zero treatment is a treatment in which the crystal structure of austenite which is not transformed into the crystal structure of martensite by the quenching treatment and is retained is transformed into martensite by cooling. The crystal structure of the retained austenite is often transformed into martensite over time, however, at this time, the volume of the sintered body changes. Therefore, a problem occurs that the size of the sintered body changes over time. Therefore, by performing the sub-zero treatment after the quenching treatment, the crystal structure of the retained austenite can be transformed into martensite partly forcibly, and thus, the occurrence of the problem that the size changes over time can be prevented.

[0166] In the cooling of the sintered body, for example, dry ice, carbon dioxide gas, liquid nitrogen, or the like is used.

[0167] In the sub-zero treatment, it is preferred that the temperature is about 0° C. or lower and the time is about 0.2 hours or more and 3 hours or less.

[0168] Further, the tempering treatment is a treatment in which the sintered body having undergone the quenching treatment is heated again at a lower temperature than in the quenching treatment. By doing this, toughness can be imparted while decreasing the hardness of the sintered body.

[0169] In the tempering treatment, it is preferred that the temperature is about 100° C. or higher and 200° C. or lower and the time is about 0.3 hours or more and 5 hours or less.

[0170] In the firing step and the respective additional treatments described above, a light element in the metal powder (in the sintered body) is volatilized, and the composition of the finally obtained sintered body slightly varies from the composition of the metal powder in some cases.

[0171] For example, the content of C in the final sintered body may change within the range of 5% or more and 100% or less (preferably within the range of 30% or more and 100% or less) of the content of C in the metal powder for powder metallurgy, which varies depending on the conditions for the step or the treatments.

[0172] Also the content of O in the final sintered body may change within the range of 1% or more and 50% or less (preferably within the range of 3% or more and 50% or less) of the content of O in the metal powder for powder metallurgy, which varies depending on the conditions for the step or the treatments.

[0173] On the other hand, as described above, the produced sintered body may be subjected to an HIP treatment as part of the additional treatments to be performed as desired, however, even if the HIP treatment is performed, a sufficient effect

is not exhibited in many cases. In the HIP treatment, the density of the sintered body can be further increased, however, the density of the sintered body obtained according to an embodiment of the invention has already been increased sufficiently at the end of the firing step in the first place. Therefore, even if the HIP treatment is further performed, further densification hardly proceeds.

[0174] In addition, in the HIP treatment, it is necessary to apply pressure to a material to be treated through a pressure medium, and therefore, the material to be treated may be contaminated, the composition or the physical properties of the material to be treated may unintendedly change accompanying the contamination, or the color of the material to be treated may change accompanying the contamination. Further, by the application of pressure, residual stress is generated or increased in the material to be treated, and a problem such as a change in shape or a decrease in dimensional accuracy may occur as the residual stress is released over time.

[0175] On the other hand, according to an embodiment of the invention, a sintered body having a sufficiently high density can be produced without performing such an HIP treatment, and therefore, a sintered body having a high density and a high strength can be obtained in the same manner as in the case where an HIP treatment is performed. Such a sintered body is less contaminated and discolored, and also an unintended change or the like in composition or physical properties occurs less, and also a problem such as a change in shape or a decrease in dimensional accuracy occurs less. Therefore, according to an embodiment of the invention, a sintered body having high mechanical strength and dimensional accuracy, and excellent durability can be efficiently produced.

[0176] Further, the sintered body produced according to an embodiment of the invention requires almost no additional treatments for enhancing the mechanical properties, and therefore, the composition and the crystal structure easily become uniform in the entire sintered body. Due to this, the sintered body has high structural anisotropy and therefore has excellent durability against a load from every direction regardless of its shape.

[0177] Herinabove, the metal powder for powder metallurgy, the compound, the granulated powder, and the sintered body according to the invention are described with reference to preferred embodiments, however, the invention is not limited thereto.

[0178] Further, the sintered body according to an embodiment of the invention is used for, for example, parts for transport machinery such as parts for automobiles, parts for bicycles, parts for railcars, parts for ships, parts for airplanes, and parts for space transport machinery (such as rockets); parts for electronic devices such as parts for personal computers and parts for mobile phone terminals; parts for electrical devices such as refrigerators, washing machines, and cooling and heating machines; parts for machines such as machine tools and semiconductor production apparatuses; parts for plants such as atomic power plants, thermal power plants, hydroelectric power plants, oil refinery plants, and chemical complexes; parts for time pieces, metallic tableware, jewels, ornaments such as frames for glasses, and other all sorts of structural parts.

## EXAMPLES

[0179] Next, examples of the invention will be described.

1. Production of Sintered Body Involving Molding by Injection Molding Method

Sample No. 1

[0180] (1) First, a metal powder having a composition shown in Table 1 produced by a water atomization method was prepared. This metal powder had an average particle diameter of 3.86  $\mu\text{m}$ , a tap density of 4.38  $\text{g}/\text{cm}^3$ , and a specific surface area of 0.24  $\text{m}^2/\text{g}$ .

[0181] The composition of the powder shown in Table 1 was identified and determined by an inductively coupled high-frequency plasma optical emission spectroscopy (ICP method). In the ICP analysis, an ICP apparatus (model: CIROS-120) manufactured by Rigaku Corporation was used. Further, in the identification and determination of C and S, a carbon-sulfur analyzer (CS-200) manufactured by LECO Corporation was used. Further, in the identification and determination of O, an oxygen-nitrogen analyzer (TC-300/EF-300) manufactured by LECO Corporation was used.

[0182] (2) Subsequently, the metal powder and a mixture (an organic binder) of polypropylene and a wax were weighed at a mass ratio of 9:1 and mixed with each other, whereby a mixed starting material was obtained.

[0183] (3) Subsequently, this mixed starting material was kneaded using a kneader, whereby a compound was obtained.

[0184] (4) Subsequently, this compound was molded using an injection molding device under the following molding conditions, whereby a molded body was produced.

[0185] Molding Conditions

[0186] Material temperature: 150° C.

[0187] Injection pressure: 11 MPa (110 kgf/cm<sup>2</sup>)

[0188] (5) Subsequently, the obtained molded body was subjected to a heat treatment (degreasing treatment) under the following degreasing conditions, whereby a degreased body was obtained.

[0189] Degreasing Conditions

[0190] Degreasing temperature: 450° C.

[0191] Degreasing time: 2 hours (retention time at the degreasing temperature)

[0192] Degreasing atmosphere: nitrogen atmosphere

[0193] (6) Subsequently, the obtained degreased body was fired under the following firing conditions, whereby a sintered body was obtained. The shape of the sintered body was determined to be a cylinder with a diameter of 10 mm and a thickness of 5 mm.

tered body was obtained. The shape of the sintered body was determined to be a cylinder with a diameter of 10 mm and a thickness of 5 mm.

[0194] Firing Conditions

[0195] Firing temperature: 1150° C.

[0196] Firing time: 3 hours (retention time at the firing temperature)

[0197] Firing atmosphere: argon atmosphere

[0198] (7) Subsequently, the obtained sintered body was subjected to a quenching treatment under the following conditions.

[0199] Quenching Treatment Conditions

[0200] Quenching temperature: 980° C.

[0201] Quenching time: 4 hours

[0202] Quenching atmosphere: argon atmosphere

[0203] Cooling Method: water cooling

[0204] (8) Subsequently, the sintered body having undergone the quenching treatment was subjected to a sub-zero treatment under the following conditions.

[0205] Sub-zero Treatment Conditions

[0206] Sub-zero treatment temperature: -196° C.

[0207] Sub-zero treatment time: 2 hours

[0208] (9) Subsequently, the sintered body having undergone the sub-zero treatment was subjected to a tempering treatment under the following conditions.

[0209] Tempering Treatment Conditions

[0210] Tempering treatment temperature: 210° C.

[0211] Tempering treatment time: 4 hours

Sample Nos. 2 to 36

[0212] Sintered bodies were obtained in the same manner as the method for producing the sintered body of the sample No. 1 except that the composition and the like of the metal powder for powder metallurgy were changed as shown in Table 1, respectively. The sintered body of the sample No. 36 is obtained by further subjecting the sintered body of the sample No. 35 to an HIP treatment under the following conditions to increase the density of the sintered body. Further, the sintered bodies of the sample Nos. 28 to 30 were obtained by using the metal powder produced by a gas atomization method, respectively, and indicated by "Gas" in the column of remarks in Table 1.

[0213] HIP Treatment Conditions

[0214] Heating temperature: 1100° C.

[0215] Heating time: 2 hours

[0216] Applied pressure: 100 MPa

TABLE 1

Sample	Composition of alloy												Zr/Nb	Zr + Nb Mass	(Zr + Nb)/ Si	(Zr + Nb)/ C	Mn + Ni Mass	Remarks
	No.	—	Cr	C	Si	Zr	Nb	Mn	Ni	Cu	O	Fe						
No. 1	Example	12.88	0.90	0.73	0.07	0.07	0.10	0.07	<0.01	0.27	Remainder	1.00	0.14	0.19	0.16	0.17		
No. 2	Example	14.24	0.28	0.58	0.09	0.05	0.12	0.05	<0.01	0.24	Remainder	1.80	0.14	0.24	0.50	0.17		
No. 3	Example	11.63	1.13	0.78	0.05	0.06	0.07	0.05	<0.01	0.31	Remainder	0.83	0.11	0.14	0.10	0.12		
No. 4	Example	13.37	0.85	0.64	0.10	0.05	0.08	0.10	<0.01	0.25	Remainder	2.00	0.15	0.23	0.18	0.18		
No. 5	Example	12.54	0.98	0.75	0.05	0.10	0.11	0.06	<0.01	0.29	Remainder	0.50	0.15	0.20	0.15	0.17		
No. 6	Example	11.23	0.47	0.52	0.12	0.04	0.12	0.12	<0.01	0.22	Remainder	3.00	0.16	0.31	0.34	0.24		
No. 7	Example	14.87	0.98	0.69	0.04	0.12	0.09	0.05	<0.01	0.41	Remainder	0.33	0.16	0.23	0.16	0.14		
No. 8	Example	12.64	0.74	0.77	0.11	0.09	0.08	0.06	<0.01	0.30	Remainder	1.22	0.20	0.26	0.27	0.16		
No. 9	Example	13.89	0.65	0.51	0.05	0.05	0.11	0.05	<0.01	0.28	Remainder	1.00	0.10	0.20	0.15	0.16		
No. 10	Example	10.56	0.78	0.32	0.08	0.09	0.18	0.15	<0.01	0.25	Remainder	0.89	0.17	0.53	0.22	0.33		

TABLE 1-continued

Metal powder for powder metallurgy																	
Sample	Composition of alloy										Zr/Nb	Zr + Nb Mass	(Zr + Nb)/ Si	(Zr + Nb)/ C	Mn + Ni Mass	Remarks	
	No.	—	Cr	C	Si	Zr	Nb	Mn	Ni	Cu	O	Fe	—	%	—	%	—
No. 11	Example	16.26	1.05	0.62	0.08	0.06	0.05	0.07	<0.01	0.29	Remainder	1.33	0.14	0.23	0.13	0.12	
No. 12	Example	19.74	0.92	0.88	0.10	0.10	0.04	0.08	<0.01	0.48	Remainder	1.00	0.20	0.23	0.22	0.12	
No. 13	Example	23.69	0.41	0.44	0.08	0.08	0.07	0.06	<0.01	0.68	Remainder	1.00	0.16	0.36	0.39	0.13	
No. 14	Example	10.20	0.55	0.65	0.14	0.04	0.09	0.06	<0.01	0.19	Remainder	3.50	0.18	0.28	0.33	0.15	
No. 15	Example	12.91	0.81	0.68	0.03	0.14	0.07	0.07	<0.01	0.27	Remainder	0.21	0.17	0.25	0.21	0.14	
No. 16	Example	11.89	0.88	0.75	0.05	0.03	0.09	0.07	<0.01	0.23	Remainder	1.67	0.08	0.11	0.09	0.16	
No. 17	Example	12.78	0.74	0.61	0.12	0.12	0.11	0.06	<0.01	0.25	Remainder	1.00	0.24	0.39	0.32	0.17	
No. 18	Example	12.80	0.87	0.75	0.07	0.08	0.01	0.06	<0.01	0.24	Remainder	0.88	0.15	0.20	0.17	0.07	
No. 19	Example	12.80	0.87	0.75	0.07	0.08	0.30	0.05	<0.01	0.24	Remainder	0.88	0.15	0.20	0.17	0.35	
No. 20	Example	12.80	0.87	0.75	0.07	0.08	1.00	0.60	<0.01	0.24	Remainder	0.88	0.15	0.20	0.17	1.60	
No. 21	Example	12.88	0.90	0.73	0.07	0.07	0.10	0.20	<0.01	0.27	Remainder	1.00	0.14	0.19	0.16	0.30	
No. 22	Example	12.75	0.93	0.71	0.01	0.07	0.11	0.07	<0.01	0.29	Remainder	0.14	0.08	0.11	0.09	0.18	
No. 23	Example	12.94	1.02	0.79	0.05	0.01	0.09	0.06	<0.01	0.31	Remainder	5.00	0.06	0.08	0.06	0.15	
No. 24	Example	11.56	0.63	0.54	0.21	0.07	0.11	0.08	<0.01	0.38	Remainder	3.00	0.28	0.52	0.44	0.19	
No. 25	Example	14.35	0.47	0.77	0.06	0.19	0.05	0.04	<0.01	0.41	Remainder	0.32	0.25	0.32	0.53	0.09	
No. 26	Example	12.11	0.51	0.53	0.20	0.17	0.11	0.08	<0.01	0.27	Remainder	1.18	0.37	0.70	0.73	0.19	
No. 27	Example	12.78	0.78	0.72	0.32	0.41	0.12	0.08	<0.01	0.31	Remainder	0.78	0.73	1.01	0.94	0.20	
No. 28	Example	13.37	0.85	0.64	0.10	0.05	0.08	0.10	<0.01	0.25	Remainder	2.00	0.15	0.23	0.18	0.18	
No. 29	Example	12.54	0.98	0.75	0.05	0.10	0.11	0.06	<0.01	0.29	Remainder	0.50	0.15	0.20	0.15	0.17	
No. 30	Example	11.23	0.47	0.52	0.12	0.04	0.12	0.12	<0.01	0.22	Remainder	3.00	0.16	0.31	0.34	0.24	
No. 31	Comparative Example	12.54	0.95	0.82	0.00	0.05	0.12	0.08	<0.01	0.25	Remainder	0.00	0.05	0.06	0.05	0.20	
No. 32	Comparative Example	12.95	0.76	0.78	0.04	0.00	0.08	0.10	<0.01	0.31	Remainder	—	0.04	0.05	0.05	0.18	
No. 33	Comparative Example	13.25	0.45	0.42	0.68	0.05	0.08	0.06	<0.01	0.27	Remainder	13.60	0.73	1.74	1.62	0.14	
No. 34	Comparative Example	13.58	0.58	0.36	0.03	0.62	0.07	0.05	<0.01	0.32	Remainder	0.05	0.65	1.81	1.12	0.12	
No. 35	Comparative Example	13.50	1.00	0.75	0.00	0.00	0.12	0.11	<0.01	0.33	Remainder	—	0.00	0.00	0.00	0.23	
No. 36	Comparative Example	13.50	1.00	0.75	0.00	0.00	0.12	0.11	<0.01	0.33	Remainder	—	0.00	0.00	0.00	HIP	

[0217] In Table 1, among the metal powders for powder metallurgy and the sintered bodies of the respective sample Nos., those corresponding to embodiments of the invention are indicated by “Example”, and those not corresponding to the embodiments of the invention are indicated by “Comparative Example”.

Sample Nos. 37 to 67

[0218] Sintered bodies were obtained in the same manner as the method for producing the sintered body the sample No. 1 except that the composition and the like of the metal powder for powder metallurgy were changed as shown in Table 2, respectively.

The sintered body of the sample No. 67 is obtained by further subjecting the sintered body of the sample No. 66 to an HIP treatment under the following conditions to increase the density of the sintered body. Further, the sintered bodies of the sample Nos. 57 to 59 were obtained by using the metal powder produced by a gas atomization method, respectively, and indicated by “Gas” in the column of remarks in Table 2.

#### [0219] HIP Treatment Conditions

[0220] Heating temperature: 1100°C.

[0221] Heating time: 2 hours

[0222] Applied pressure: 100 MPa

TABLE 2

Metal powder for powder metallurgy																	
Sample	Composition of alloy										Zr/Nb	Zr + Nb Mass	(Zr + Nb)/ Si	(Zr + Nb)/ C	Mn + Ni Mass	Remarks	
	No.	—	Cr	C	Si	Zr	Nb	Mn	Ni	Cu	O	Fe	—	%	—	%	—
No. 37	Example	17.00	1.00	0.80	0.07	0.07	0.10	0.20	<0.01	0.27	Remainder	1.00	0.14	0.18	0.14	0.30	
No. 38	Example	16.78	0.98	0.58	0.09	0.05	0.12	0.25	<0.01	0.24	Remainder	1.80	0.14	0.24	0.14	0.37	
No. 39	Example	17.69	1.05	0.78	0.05	0.06	0.07	0.05	<0.01	0.31	Remainder	0.83	0.11	0.14	0.10	0.12	
No. 40	Example	16.23	1.04	0.52	0.12	0.04	0.09	0.15	<0.01	0.22	Remainder	3.00	0.16	0.31	0.15	0.24	
No. 41	Example	16.87	1.09	0.69	0.04	0.12	0.09	0.05	<0.01	0.41	Remainder	0.33	0.16	0.23	0.15	0.14	
No. 42	Example	17.64	0.68	0.77	0.11	0.09	0.08	0.08	<0.01	0.30	Remainder	1.22	0.20	0.26	0.29	0.16	
No. 43	Example	17.89	0.72	0.51	0.05	0.05	0.11	0.05	<0.01	0.28	Remainder	1.00	0.10	0.20	0.14	0.16	

TABLE 2-continued

Sample	Metal powder for powder metallurgy												Zr + Nb Mass	(Zr + Nb)/ Si	(Zr + Nb)/ C	Mn + Ni Mass	Remarks
	Composition of alloy																
	No.	—	Cr	C	Si	Zr	Nb	Mn	Ni	Cu	O	Fe	—	%	—	—	%
No. 44	Example	16.50	1.12	0.32	0.08	0.09	0.18	0.15	<0.01	0.25	Remainder	0.89	0.17	0.53	0.15	0.33	
No. 45	Example	16.26	1.05	0.62	0.08	0.06	0.05	0.07	<0.01	0.29	Remainder	1.33	0.14	0.23	0.13	0.12	
No. 46	Example	17.74	0.96	0.88	0.10	0.10	0.04	0.08	<0.01	0.48	Remainder	1.00	0.20	0.23	0.21	0.12	
No. 47	Example	16.69	0.98	0.44	0.08	0.08	0.07	0.09	<0.01	0.57	Remainder	1.00	0.16	0.36	0.16	0.16	
No. 48	Example	17.81	0.96	0.75	0.07	0.08	0.01	0.06	<0.01	0.24	Remainder	0.88	0.15	0.20	0.16	0.07	
No. 49	Example	16.56	0.78	0.84	0.07	0.08	1.00	0.50	<0.01	0.24	Remainder	0.88	0.15	0.18	0.19	1.60	
No. 50	Example	17.56	0.95	0.81	0.01	0.07	0.12	0.08	<0.01	0.31	Remainder	0.14	0.08	0.10	0.08	0.20	
No. 51	Example	16.94	1.06	0.69	0.05	0.01	0.10	0.07	<0.01	0.29	Remainder	5.00	0.06	0.07	0.06	0.17	
No. 52	Example	17.58	0.78	0.54	0.21	0.07	0.11	0.08	<0.01	0.38	Remainder	3.00	0.28	0.52	0.36	0.19	
No. 53	Example	16.35	0.76	0.77	0.06	0.19	0.05	0.04	<0.01	0.41	Remainder	0.32	0.25	0.32	0.33	0.09	
No. 54	Example	17.78	0.99	0.72	0.41	0.35	0.13	0.09	<0.01	0.31	Remainder	1.17	0.76	1.06	0.77	0.22	
No. 55	Example	13.25	0.18	0.79	0.07	0.07	0.15	0.21	<0.01	0.25	Remainder	1.00	0.14	0.16	0.78	0.36	
No. 56	Example	13.02	0.36	0.81	0.08	0.06	0.08	0.19	<0.01	0.19	Remainder	1.33	0.14	0.17	0.39	0.27	
No. 57	Example	17.00	1.00	0.80	0.07	0.07	0.10	0.20	<0.01	0.27	Remainder	1.00	0.14	0.18	0.14	0.30	Gas
No. 58	Example	16.78	0.98	0.58	0.09	0.05	0.12	0.25	<0.01	0.24	Remainder	1.80	0.14	0.24	0.14	0.37	Gas
No. 59	Example	17.69	1.05	0.78	0.05	0.06	0.07	0.05	<0.01	0.31	Remainder	0.83	0.11	0.14	0.10	0.12	Gas
No. 60	Comparative Example	17.54	0.99	0.82	0.00	0.06	0.11	0.09	<0.01	0.29	Remainder	0.00	0.06	0.07	0.06	0.20	
No. 61	Comparative Example	16.95	1.05	0.78	0.07	0.00	0.07	0.12	<0.01	0.32	Remainder	—	0.07	0.09	0.07	0.19	
No. 62	Comparative Example	17.00	1.12	0.42	0.59	0.04	0.06	0.07	<0.01	0.28	Remainder	14.75	0.63	1.50	0.56	0.13	
No. 63	Comparative Example	17.45	1.14	0.36	0.06	0.74	0.07	0.05	<0.01	0.35	Remainder	0.08	0.80	2.22	0.70	0.13	
No. 64	Comparative Example	13.25	0.18	0.79	0.04	0.00	0.15	0.21	<0.01	0.25	Remainder	—	0.04	0.05	0.22	0.36	
No. 65	Comparative Example	13.02	0.36	0.81	0.05	0.00	0.08	0.19	<0.01	0.19	Remainder	—	0.05	0.06	0.14	0.27	
No. 66	Comparative Example	16.28	1.04	0.25	0.00	0.00	0.31	0.00	<0.01	0.42	Remainder	—	0.00	0.00	0.00	0.31	
No. 67	Comparative Example	16.28	1.04	0.25	0.00	0.00	0.31	0.00	<0.01	0.42	Remainder	—	0.00	0.00	0.00	0.31	HIP

[0223] In Table 2, among the metal powders for powder metallurgy and the sintered bodies of the respective sample Nos., those corresponding to embodiments of the invention are indicated by “Example”, and those not corresponding to embodiments of the invention are indicated by “Comparative Example”.

## 2. Evaluation of Sintered Body Involving Molding by Injection Molding Method

### 2.1 Evaluation of Relative Density

[0224] With respect to the sintered bodies of the respective sample Nos., the sintered density was measured in accordance with the method for measuring the density of sintered metal materials specified in JIS Z 2501, and also the relative density of each sintered body was calculated with reference to the true density of the metal powder for powder metallurgy used for producing each sintered body.

[0225] The calculated results are shown in Tables 3 and 4.

### 2.2 Evaluation of Vickers Hardness

[0226] With respect to the sintered bodies of the respective sample Nos., the Vickers hardness was measured in accordance with the Vickers hardness testing method specified in JIS Z 2244.

[0227] The measurement results are shown in Tables 3 and 4.

### 2.3 Evaluation of Tensile Strength, 0.2% Proof Stress, and Elongation

[0228] With respect to the sintered bodies of the respective sample Nos., the tensile strength, 0.2% proof stress, and elongation were measured in accordance with the metal material tensile testing method specified in JIS Z 2241.

[0229] Then, the measured values of these physical properties were evaluated according to the following evaluation criteria.

#### Evaluation Criteria for Tensile Strength

[0230] A: The tensile strength of the sintered body is very high (1800 MPa or more).

[0231] B: The tensile strength of the sintered body is high (1600 MPa or more and less than 1800 MPa).

[0232] C: The tensile strength of the sintered body is slightly high (1400 MPa or more and less than 1600 MPa).

[0233] D: The tensile strength of the sintered body is slightly low (1200 MPa or more and less than 1400 MPa).

[0234] E: The tensile strength of the sintered body is low (1000 MPa or more and less than 1200 MPa).

[0235] F: The tensile strength of the sintered body is very low (800 MPa or more and less than 1000 MPa).

[0236] G: The tensile strength of the sintered body is particularly low (less than 800 MPa).

## Evaluation Criteria for 0.2% Proof Stress

[0237] A: The 0.2% proof stress of the sintered body is very high (1200 MPa or more).

[0238] B: The 0.2% proof stress of the sintered body is high (1100 MPa or more and less than 1200 MPa).

[0239] C: The 0.2% proof stress of the sintered body is slightly high (1000 MPa or more and less than 1100 MPa).

[0240] D: The 0.2% proof stress of the sintered body is slightly low (900 MPa or more and less than 1000 MPa).

[0241] E: The 0.2% proof stress of the sintered body is low (800 MPa or more and less than 900 MPa).

[0242] F: The 0.2% proof stress of the sintered body is very low (700 MPa or more and less than 800 MPa).

[0243] G: The 0.2% proof stress of the sintered body is particularly low (less than 700 MPa).

## Evaluation Criteria for Elongation

[0244] A: The elongation of the sintered body is very large (7% or more).

[0245] B: The elongation of the sintered body is large (6% or more and less than 70).

[0246] C: The elongation of the sintered body is slightly large (5% or more and less than 6%).

[0247] D: The elongation of the sintered body is slightly small (4% or more and less than 5%).

[0248] E: The elongation of the sintered body is small (3% or more and less than 4%).

[0249] F: The elongation of the sintered body is very small (2% or more and less than 3%).

[0250] G: The elongation of the sintered body is particularly small (less than 2%).

[0251] The above evaluation results are shown in Tables 3 and 4.

TABLE 3

Sample No.	—	Metal powder Average	Evaluation results of sintered body					
			particle diameter $\mu\text{m}$	Relative density %	Vickers hardness —	Tensile strength —	0.2% proof stress —	Elongation —
No. 1	Example	3.86	99.5	700	A	A	A	A
No. 2	Example	3.79	98.2	670	B	B	B	B
No. 3	Example	3.84	98.4	650	B	B	B	B
No. 4	Example	3.92	99.3	680	A	A	A	A
No. 5	Example	4.02	99.4	690	A	A	A	A
No. 6	Example	3.68	97.8	580	B	B	B	B
No. 7	Example	3.77	98.2	590	B	B	B	B
No. 8	Example	3.81	98.8	610	A	A	A	B
No. 9	Example	3.85	98.9	600	A	A	A	B
No. 10	Example	4.05	98.5	570	B	B	B	B
No. 11	Example	3.97	98.9	630	A	A	A	B
No. 12	Example	3.92	93.6	620	B	B	B	B
No. 13	Example	3.74	97.5	680	B	B	B	C
No. 14	Example	3.81	97.2	520	B	B	B	B
No. 15	Example	3.86	97.4	540	B	B	B	B
No. 16	Example	3.88	97.1	600	B	B	B	B
No. 17	Example	3.76	97.2	610	B	B	B	B
No. 18	Example	3.84	97.0	510	C	C	B	B
No. 19	Example	3.84	97.2	550	B	B	C	C
No. 20	Example	3.86	96.8	505	C	C	C	C
No. 21	Example	3.76	97.3	610	B	B	B	B
No. 22	Example	3.77	95.8	620	D	D	D	B
No. 23	Example	3.94	96.2	630	D	C	B	B
No. 24	Example	3.05	95.7	520	D	D	D	D
No. 25	Example	3.12	95.6	510	D	D	D	D
No. 26	Example	3.09	95.5	505	D	D	D	D
No. 27	Example	2.85	95.1	495	D	D	D	D
No. 28	Example	7.84	99.1	670	A	A	A	A
No. 29	Example	8.04	99.2	680	A	A	A	A
No. 30	Example	7.23	98.3	590	B	B	B	B
No. 31	Comparative Example	3.67	93.8	460	F	F	F	C
No. 32	Comparative Example	3.48	94.5	485	E	C	C	C
No. 33	Comparative Example	2.97	94.8	490	E	E	D	D
No. 34	Comparative Example	3.05	93.2	455	F	F	D	D
No. 35	Comparative Example	2.16	93.1	480	F	F	F	F
No. 36	Comparative Example	3.04	99.2	660	A	A	B	B

TABLE 4

Sample No.	—	Metal powder Average particle diameter μm	Evaluation results of sintered body				
			Relative density %	Vickers hardness —	Tensile strength —	0.2% proof stress —	Elongation —
No. 37	Example	4.15	99.5	825	A	A	A
No. 38	Example	4.03	99.6	830	A	A	A
No. 39	Example	4.25	98.3	750	B	B	B
No. 40	Example	4.05	97.6	735	B	B	B
No. 41	Example	3.98	97.5	730	B	B	B
No. 42	Example	4.23	99.1	610	B	B	B
No. 43	Example	5.36	99.2	600	B	B	B
No. 44	Example	4.05	97.6	770	B	B	B
No. 45	Example	4.14	99.3	825	A	A	B
No. 46	Example	4.58	98.4	720	B	B	B
No. 47	Example	6.35	98.9	780	B	B	C
No. 48	Example	4.45	99.1	740	C	C	B
No. 49	Example	10.8	98.9	685	C	C	C
No. 50	Example	4.78	95.9	710	D	D	B
No. 51	Example	4.69	96.4	720	D	C	B
No. 52	Example	4.36	95.7	620	D	D	D
No. 53	Example	4.12	95.6	610	D	D	D
No. 54	Example	15.4	95.4	690	D	D	D
No. 55	Example	4.23	99.1	610	B	B	B
No. 56	Example	3.87	99.3	630	A	A	A
No. 57	Example	8.31	99.3	815	A	A	A
No. 58	Example	8.06	99.4	820	A	A	A
No. 59	Example	8.52	98.1	740	B	B	B
No. 60	Comparative Example	4.58	93.7	660	F	F	C
No. 61	Comparative Example	4.49	94.4	685	E	C	C
No. 62	Comparative Example	4.79	94.7	680	E	E	D
No. 63	Comparative Example	4.56	93.6	665	F	F	D
No. 64	Comparative Example	4.35	94.9	575	F	F	F
No. 65	Comparative Example	3.78	94.6	560	E	E	E
No. 66	Comparative Example	2.28	93.3	480	B	B	F
No. 67	Comparative Example	2.28	98.8	645	A	A	B

[0252] As apparent from Tables 3 and 4, it was confirmed that each of the sintered bodies obtained in the respective Examples has a higher relative density and also a higher Vickers hardness than the sintered bodies obtained in the respective Comparative Examples (excluding the sintered body having undergone the HIP treatment). Further, it was also confirmed that there is a significant difference in properties such as tensile strength, 0.2% proof stress, and elongation between the sintered bodies obtained in the respective Examples and the sintered bodies obtained in the respective Comparative Examples (excluding the sintered body having undergone the HIP treatment).

### 3. Production of Sintered Body Involving Molding by Compact Molding Method

Sample No. 68

[0253] (1) First, a metal powder having a composition shown in Table 5 was produced by a water atomization method in the same manner as in the case of the sample No. 1.

[0254] (2) Subsequently, the metal powder was granulated by a spray drying method. The binder used at this time was polyvinyl alcohol, which was used in an amount of 1 part by

mass with respect to 100 parts by mass of the metal powder. Further, a solvent (ion exchanged water) was used in an amount of 50 parts by mass with respect to 1 part by mass of polyvinyl alcohol. In this manner, a granulated powder having an average particle diameter of 50 μm was obtained.

[0255] (3) Subsequently, this granulated powder was molded using a press molding device under the following molding conditions, whereby a molded body was produced. The shape of the molded body was determined to be a cube with a side length of 20 mm.

#### Molding Conditions

[0256] Material temperature: 90° C.

[0257] Molding pressure: 600 MPa (6 t/cm<sup>2</sup>)

[0258] (4) Subsequently, the obtained molded body was subjected to a heat treatment (degreasing treatment) under the following degreasing conditions, whereby a degreased body was obtained.

#### Degreasing Conditions

[0260] Degreasing temperature: 450° C.

[0261] Degreasing time: 2 hours (retention time at the degreasing temperature)

[0262] Degreasing atmosphere: nitrogen atmosphere

[0263] (5) Subsequently, the obtained degreased body was fired under the following firing conditions, whereby a sintered body was obtained.

[0264] Firing Conditions

[0265] Firing temperature: 1150° C.

[0266] Firing time: 3 hours (retention time at the firing temperature)

[0267] Firing atmosphere: argon atmosphere

[0268] (6) Subsequently, the obtained sintered body was subjected to a quenching treatment, a sub-zero treatment, and a tempering treatment in the same manner as in the case of the sample No. 1.

Sample Nos. 69 to 84

[0269] Sintered bodies were obtained in the same manner as in the case of the sample No. 68 except that the composition and the like of the metal powder for powder metallurgy were changed as shown in Table 5, respectively. The sintered body of the sample No. 84 is obtained by further subjecting the sintered body of the sample No. 83 to an HIP treatment under the following conditions to increase the density of the sintered body.

[0270] HIP Treatment Conditions

[0271] Heating temperature: 1100° C.

[0272] Heating time: 2 hours

[0273] Applied pressure: 100 MPa

[0274] In Table 5, among the metal powders for powder metallurgy and the sintered bodies of the respective sample Nos., those corresponding to embodiments of the invention are indicated by "Example", and those not corresponding to embodiments of the invention are indicated by "Comparative Example".

4. Evaluation of Sintered Body Involving Molding by Compact Molding Method

4.1 Evaluation of Relative Density

[0275] With respect to the sintered bodies of the respective sample Nos., the sintered density was measured in accordance with the method for measuring the density of sintered metal materials specified in JIS Z 2501, and also the relative density of each sintered body was calculated with reference to the true density of the metal powder for powder metallurgy used for producing each sintered body.

[0276] The calculated results are shown in Table 6.

4.2 Evaluation of Vickers Hardness

[0277] With respect to the sintered bodies of the respective sample Nos., the Vickers hardness was measured in accordance with the Vickers hardness testing method specified in JIS Z 2244.

TABLE 5

Sample	No.	Composition of alloy										Zr/Nb	Zr + Nb Mass	(Zr + Nb)/Si	(Zr + Nb)/C	Mn + Ni Mass	Remarks
		—	Cr	C	Si	Zr	Nb	Mn	Ni	Cu	O						
		—	—	—	—	—	—	—	—	—	—						
No. 68	Example	12.88	0.90	0.73	0.07	0.07	0.10	0.07	<0.01	0.27	Remainder	1.00	0.14	0.19	0.16	0.17	Compact molding
No. 69	Example	14.24	0.28	0.58	0.09	0.05	0.12	0.05	<0.01	0.24	Remainder	1.80	0.14	0.24	0.50	0.17	Compact molding
No. 70	Example	11.63	1.13	0.78	0.05	0.06	0.07	0.05	<0.01	0.31	Remainder	0.83	0.11	0.14	0.10	0.12	Compact molding
No. 71	Example	13.37	0.85	0.54	0.10	0.05	0.08	0.10	<0.01	0.25	Remainder	2.00	0.15	0.23	0.18	0.18	Compact molding
No. 72	Example	12.54	0.98	0.75	0.05	0.10	0.11	0.06	<0.01	0.29	Remainder	0.50	0.15	0.20	0.15	0.17	Compact molding
No. 73	Example	11.23	0.47	0.52	0.12	0.04	0.12	0.12	<0.01	0.22	Remainder	3.00	0.16	0.31	0.34	0.24	Compact molding
No. 74	Example	14.87	0.98	0.69	0.04	0.12	0.09	0.05	<0.01	0.41	Remainder	0.33	0.16	0.23	0.16	0.14	Compact molding
No. 75	Example	12.64	0.74	0.77	0.11	0.09	0.08	0.08	<0.01	0.30	Remainder	1.22	0.20	0.26	0.27	0.16	Compact molding
No. 76	Example	13.89	0.65	0.51	0.05	0.05	0.11	0.05	<0.01	0.28	Remainder	1.00	0.10	0.20	0.15	0.16	Compact molding
No. 77	Example	10.56	0.78	0.32	0.08	0.09	0.18	0.15	<0.01	0.25	Remainder	0.89	0.17	0.53	0.22	0.33	Compact molding
No. 78	Example	16.26	1.05	0.62	0.08	0.06	0.05	0.07	<0.01	0.29	Remainder	1.33	0.14	0.23	0.13	0.12	Compact molding
No. 79	Comparative Example	12.54	0.95	0.82	0.00	0.05	0.12	0.08	<0.01	0.25	Remainder	0.00	0.05	0.06	0.05	0.20	Compact molding
No. 80	Comparative Example	12.95	0.76	0.78	0.04	0.00	0.08	0.10	<0.01	0.31	Remainder	—	0.04	0.05	0.05	0.18	Compact molding
No. 81	Comparative Example	13.25	0.45	0.42	0.68	0.05	0.08	0.05	<0.01	0.27	Remainder	13.60	0.73	1.74	1.62	0.14	Compact molding
No. 82	Comparative Example	13.58	0.58	0.36	0.03	0.62	0.07	0.05	<0.01	0.32	Remainder	0.05	0.65	1.81	1.12	0.12	Compact molding
No. 83	Comparative Example	13.50	1.00	0.75	0.00	0.00	0.12	0.11	<0.01	0.33	Remainder	—	0.00	0.00	0.00	0.23	Compact molding
No. 84	Comparative Example	13.50	1.00	0.75	0.00	0.00	0.12	0.11	<0.01	0.33	Remainder	—	0.00	0.00	0.00	0.23	HIP

[0278] The measurement results are shown in Table 6.

#### 4.3 Evaluation of Tensile Strength, 0.2% Proof Stress, and Elongation

[0279] With respect to the sintered bodies of the respective sample Nos., the tensile strength, 0.2% proof stress, and elongation were measured in accordance with the metal material tensile testing method specified in JIS Z 2241.

[0280] Then, the measured values of the physical properties were evaluated according to the above-described evaluation criteria.

[0281] The above evaluation results are shown in Table 6.

TABLE 6

Sample No.	—	Metal powder Average particle diameter μm	Evaluation results of sintered body				
			Relative density %	Vickers hardness —	Tensile strength —	0.2% proof stress —	Elongation —
No. 68	Example	3.86	99.6	710	A	A	A
No. 69	Example	3.79	98.5	680	B	B	B
No. 70	Example	3.84	98.6	660	B	B	B
No. 71	Example	3.92	99.5	690	A	A	A
No. 72	Example	4.02	99.6	700	A	A	A
No. 73	Example	3.68	98.1	590	B	B	B
No. 74	Example	3.77	98.4	600	B	B	B
No. 75	Example	3.81	98.9	610	A	A	B
No. 76	Example	3.85	99.1	620	A	A	B
No. 77	Example	4.05	98.7	680	B	B	B
No. 78	Example	3.97	99.1	630	A	A	B
No. 79	Comparative Example	3.67	94.0	465	E	D	C
No. 80	Comparative Example	3.48	94.6	490	E	C	C
No. 81	Comparative Example	2.97	94.9	495	E	D	D
No. 82	Comparative Example	3.05	93.5	460	F	E	D
No. 83	Comparative Example	2.16	93.3	490	F	F	F
No. 84	Comparative Example	3.04	99.3	665	A	A	B

[0282] As apparent from Table 6, it was confirmed that each of the sintered bodies obtained in the respective Examples has a high relative density and also a high Vickers hardness even though the sintered bodies were obtained by sintering molded bodies formed by a compact molding method (press molding method). Further, it was also confirmed that there is a significant difference in properties such as tensile strength, 0.2% proof stress, and elongation between the sintered bodies obtained in the respective Examples and the sintered bodies obtained in the respective Comparative Examples.

[0283] Based on the above results, it was determined that in the sintered body obtained by sintering an Fe—Cr—C—Si-based alloy powder, both the density and the hardness can be increased by further adding Zr and Nb in an appropriate amount even without performing an additional treatment of increasing the density such as an HIP treatment.

[0284] Incidentally, in the sintered body having undergone an HIP treatment, both a high density and a high hardness comparable to those of the sintered bodies obtained in the respective Examples were achieved. Therefore, it was determined that according to an embodiment of the invention, the density can be increased to a level comparable to or higher than in the case where the HIP treatment is performed.

[0285] Further, the content of impurities in the metal powder for powder metallurgy obtained in each Example was measured and found to be less than 0.03% by mass in total in each metal powder.

[0286] Further, the content of C and the content of O in the sintered body of the sample No. 1 were measured again, and found to be 0.75% by mass and 0.02% by mass, respectively.

[0287] Incidentally, with respect to the sintered body of the sample No. 1, also for the sintered body before undergoing the quenching treatment, the sub-zero treatment, and the tempering treatment (the sintered body immediately after sinter-

ing), the relative density was evaluated in the same manner as in the above item 2.1, and the same value as shown in Table 3 was obtained.

[0288] The entire disclosures of Japanese Patent Application Nos. 2013-226545 filed Oct. 31, 2013, 2014-041332 filed Mar. 4, 2014, and 2014-167260 filed Aug. 20, 2014 are hereby expressly incorporated by reference herein.

What is claimed is:

1. A metal powder for powder metallurgy, comprising:  
Fe as a principal component;  
Cr in a proportion of 10% by mass or more and 30% by mass or less;  
C in a proportion of 0.15% by mass or more and 1.5% by mass or less;  
Si in a proportion of 0.3% by mass or more and 1% by mass or less;  
Zr in a proportion of 0.01% by mass or more and 0.5% by mass or less;  
Nb in a proportion of 0.01% by mass or more and 0.5% by mass or less; and  
Mn and Ni in a total proportion of 0.05% by mass or more and 1.6% by mass or less.

**2.** The metal powder for powder metallurgy according to claim **1**, wherein the metal powder has a crystal structure of martensite-based stainless steel.

**3.** The metal powder for powder metallurgy according to claim **1**, wherein a content ratio of the Zr to the Nb (Zr/Nb) is 0.3 or more and 3 or less.

**4.** The metal powder for powder metallurgy according to claim **1**, wherein a content sum of the Zr and Nb is 0.05% by mass or more and 0.6% by mass or less.

**5.** The metal powder for powder metallurgy according to claim **1**, wherein when a content sum of the Zr and the Nb is represented by (Zr+Nb), a ratio of (Zr+Nb) to the Si, (Zr+Nb)/Si, is 0.1 or more and 0.7 or less.

**6.** The metal powder for powder metallurgy according to claim **1**, wherein the Mn is contained therein in a proportion of 0.01% by mass or more and 1.25% by mass or less.

**7.** The metal powder for powder metallurgy according to claim **1**, wherein the Ni is contained therein in a proportion of 0.05% by mass or more and 0.6% by mass or less.

**8.** The metal powder for powder metallurgy according to claim **1**, wherein the metal powder has an average particle diameter of 0.5  $\mu\text{m}$  or more and 30  $\mu\text{m}$  or less.

**9.** A compound, comprising:

a metal powder for powder metallurgy including:

Fe as a principal component;

Cr in a proportion of 10% by mass or more and 30% by mass or less;

C in a proportion of 0.15% by mass or more and 1.5% by mass or less;

Si in a proportion of 0.3% by mass or more and 1% by mass or less;

Zr in a proportion of 0.01% by mass or more and 0.5% by mass or less;

Nb in a proportion of 0.01% by mass or more and 0.5% by mass or less; and

Mn and Ni in a total proportion of 0.05% by mass or more and 1.6% by mass or less; and

a binder which binds particles of the metal powder for powder metallurgy to one another.

**10.** The compound according to claim **9**, wherein the metal powder has a crystal structure of martensite-based stainless steel.

**11.** The compound according to claim **9**, wherein a content ratio of the Zr to the Nb (Zr/Nb) is 0.3 or more and 3 or less.

**12.** The compound according to claim **9**, wherein a content sum of the Zr and Nb is 0.05% by mass or more and 0.6% by mass or less.

**13.** The compound according to claim **9**, wherein when a content sum of the Zr and the Nb is represented by (Zr+Nb), a ratio of (Zr+Nb) to the Si, (Zr+Nb)/Si, is 0.1 or more and 0.7 or less.

**14.** A granulated powder, wherein the granulated powder is obtained by granulating the metal powder for powder metallurgy according to claim **1**.

**15.** A granulated powder, wherein the granulated powder is obtained by granulating the metal powder for powder metallurgy according to claim **2**.

**16.** A granulated powder, wherein the granulated powder is obtained by granulating the metal powder for powder metallurgy according to claim **3**.

**17.** A granulated powder, wherein the granulated powder is obtained by granulating the metal powder for powder metallurgy according to claim **4**.

**18.** A granulated powder, wherein the granulated powder is obtained by granulating the metal powder for powder metallurgy according to claim **5**.

**19.** A sintered body produced by sintering a metal powder for powder metallurgy containing:

Fe as a principal component;

Cr in a proportion of 10% by mass or more and 30% by mass or less;

C in a proportion of 0.15% by mass or more and 1.5% by mass or less;

Si in a proportion of 0.3% by mass or more and 1% by mass or less;

Zr in a proportion of 0.01% by mass or more and 0.5% by mass or less;

Nb in a proportion of 0.01% by mass or more and 0.5% by mass or less; and

Mn and Ni in a total proportion of 0.05% by mass or more and 1.6% by mass or less.

**20.** The sintered body according to claim **19**, wherein the sintered body has a relative density of 97% or more and a surface Vickers hardness of 570 or more.

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