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Kimura et al.

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[54] **METHOD FOR PRODUCING IRON-BASE SINTERED ALLOYS WITH HIGH DENSITY**

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Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 142,556, May 12, 1971, abandoned.

[30] **Foreign Application Priority Data**

July 12, 1971 Japan 46-51569

[52] **U.S. Cl.** **75/204,** 75/203, 75/226, 75/200

[51] **Int. Cl.** **B22f 1/00**

[58] **Field of Search** 75/200, 203, 204, 226

[56] **References Cited**

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[57] **ABSTRACT**

Iron-base sintered alloys, characterized by high density and good hardness, have been prepared by sintering a particulate material consisting of iron, carbon and metallic carbide at a temperature within the solid-liquid phase range corresponding to the composition ratio of said iron and carbon.

5 Claims, 4 Drawing Figures

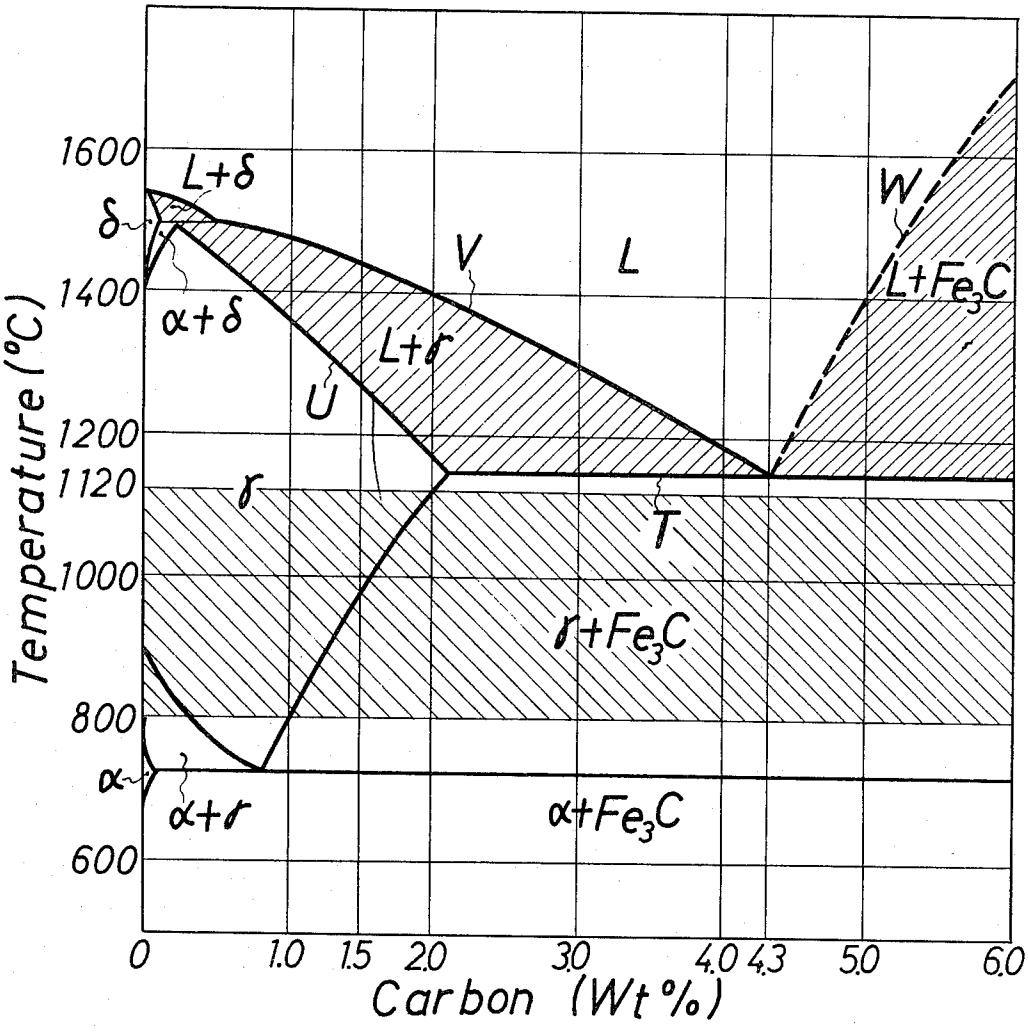


FIG.1.

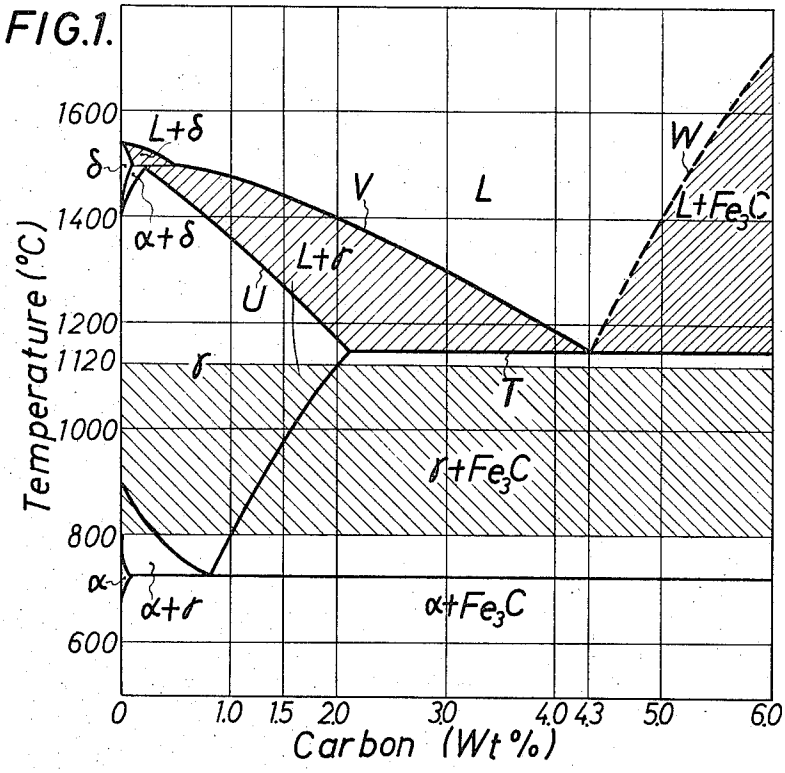


FIG.2.

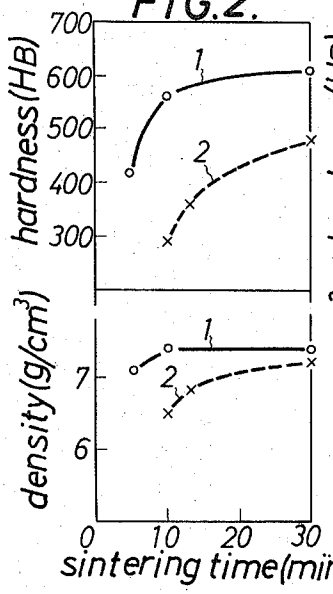


FIG.3.

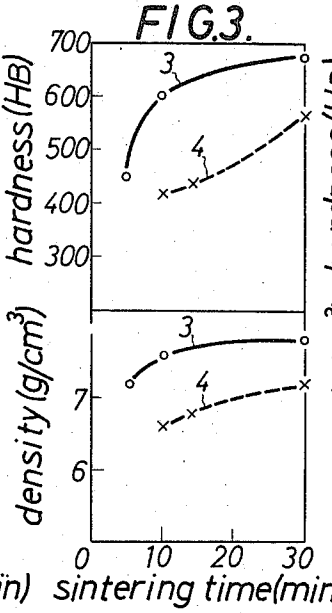
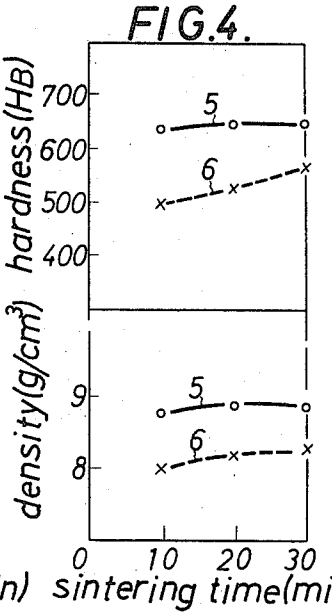


FIG.4.



METHOD FOR PRODUCING IRON-BASE SINTERED ALLOYS WITH HIGH DENSITY

CROSS-REFERENCE TO RELATED APPLICATIONS

This application is a continuation-in-part application of Ser. No. 142,556, now abandoned filed May 12, 1971, which, in turn, is entitled to priority under 35 U.S.C. 119 based on the earlier filed Japanese Application Ser. No. 45-40820, filed May 12, 1970.

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to a method for producing high density iron-base sintered alloys.

2. Description of the Prior Art

Iron-base sintered alloys are employed in a wide range of industrial applications. In conventional sintering techniques, however, the sintering is conducted at temperatures within the solid-phase range wherein the particles are totally solid. This has the disadvantage that voids will be formed between the sintered powdered particles, and hence the density of the resulting product is generally low, and the hardness is inferior.

A number of techniques have been suggested to alleviate this problem, but heretofore no reported investigation has proven to be entirely satisfactory from an industrial point of view. In one prior technique, it was suggested to sinter the particulate material under high pressure, and in another technique, it was suggested to forge the once sintered alloy at high temperatures. These methods are undersirable from an industrial point of view because they require very strong molds and very large pressing apparatus which is capable of applying sufficiently high pressures, in the order of a few hundred kg/cm^2 to several metric tons/cm^2. This requirement restricts the size of the sintered product to only those sizes which can be handled by pressing apparatus.

Another prior suggested technique was to infiltrate a low melting point molten metal into the sintered body in order to fill the void spaces within the filtered body so as to increase the product density. However, this technique is considered to be undesirably complex from an industrial point of view.

It was earlier proposed in U.S. Patent Application Ser. No. 142,556, now abandoned filed May 12, 1971, by the same applicants as herein, to produce high density iron-base sintered alloys by sintering a particulate material of iron-base alloy particles or iron-base alloy forming particles at a temperature within the range at which said particulate material coexists in a solid and liquid phase. It is the intent of the present invention to provide certain improvements to said process.

SUMMARY OF THE INVENTION

Accordingly, it is one object of this invention to provide high density sintered iron-base alloys.

Another object of the present invention is to provide a simplified method whereby a sintered iron-base alloy, which is characterized by improved density and hardness, can be prepared within a short period of time.

A still further object of this invention is to provide a method for producing a sintered iron-base alloy without the requirement for high pressures either during or subsequent to the sintering process.

A further object of the invention is to provide a method for producing iron-base sintered alloy articles.

These and other objects, as will hereinafter become more readily apparent, have been attained by forming a particulate mixture of iron and carbon, and a metallic-carbide powder (hereinafter referred to as the metal source) and then heating said particulate mixture in the solid-liquid phase temperature range corresponding to the composition ratio of the iron and carbon content. In this sintering operation, the particles in the particulate material are brought into close mutual contact so that a high density product is obtained. Voids are substantially eliminated and a high density sintered alloy is obtainable. Since a carbide powder is used as the metal source, only a relatively short period of time is required to reach the solid-liquid phase condition. As an additional embodiment of this invention, high pressures may be used during sintering to obtain an even higher density product.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 shows an equilibrium diagram of the iron-carbon alloy;

FIGS. 2,3,and 4 are graphs showing the relationship between time and hardness of a sintered body obtained according to this invention.

DETAILED DESCRIPTION OF THE INVENTION

The solid-liquid phase temperature range is that temperature range in which a solid phase and a liquid phase coexist in equilibrium. In determining the appropriate temperature range from a phase diagram, such as is shown in FIG. 1, the carbon in the metallic carbide is not considered to be included in the carbon content.

Referring more specifically to FIG. 1, the abscissa represents the carbon content by weight percent and the ordinate represents the temperature in °C.

The solid-liquid phase range is defined as the $L + \gamma$ phase range and the $L + \delta$ phase range, latched to the left downwardly in the upper left side of said FIG. 1. The temperature range corresponding to the carbon content in said $L + \gamma$ phase and $L + \delta$ phase is the solid-liquid phase temperature range in which the sintering operation of the present invention is carried out.

It is generally known that a solid-liquid phase temperature range exists when the carbon content is increased beyond 4.3 percent. In this instance, however, the carbon in excess of 4.3 percent will tend to float to the surface of the molten iron-carbon alloy in the liquid phase condition, so that it is impossible to obtain a uniform material. Therefore, the actual border line between the solid-liquid phase and the liquid phase is not precise and the existence of this imprecise border is shown by the dotted line W in FIG. 1.

In applicant's copending U.S. Application Ser. No. 142,556, now abandoned the particulate material including a carbon content of greater than 4.3 percent is sintered at a temperature of higher than the solid-phase line T (about 1,147°C.) to obtain a sintered iron base alloy having the same composition as the particulate material. It was recognized that there is an $L + Fe_3C$ phase, hatched to the left and downwardly in the upper right of FIG. 1, in which the liquid phase and the cementite coexist in equilibrium. This $L + Fe_3C$ phase range is also an applicable range in the present invention. The range below the lines T and U, which are the lower boundaries of the solid-liquid phase range, represent the solid-phase range. The temperature range

(800°C. – 1,120°C.) shown by the hatched lines extending downwardly and to the right, is the conventional sintering temperature.

In the case described above, when the particulate mixture consists of 87.3 percent by weight iron (Fe) powder, 2.7 percent by weight graphite (C) powder, and 10 percent by weight chromium carbide powder, the composition of iron and carbon is Fe - 3%C. The solid-liquid phase temperature range is therefore from 1,147°C. to 1,300°C. as apparent from FIG. 1. If the particulate mixture is heated to the solid-liquid phase temperature, at first the graphite in the particulate mixture is diffused into the iron powder, the Fe 3%C alloy composition is formed in a solid phase, and then the alloy is transformed into the solid-liquid phase to accomplish sintering.

If chromium carbide is used as the metal carbide, since it has a very high melting point, during sintering it will remain in the solid state. Particles of chromium carbide will therefore be dispersed among the Fe-3%C alloy, when that alloy is in the solid-liquid phase condition. Diffusion will occur between the chromium carbide particles and the Fe-3%C alloy during the heating operation to form an alloy of iron, chromium and carbon.

If the particulate mixture is composed of iron powder, carbon powder, and chromium carbide powder, the time required to reach the solid-liquid phase is equal to the time required for iron and carbon to mutually diffuse and be converted into an iron-carbon alloy. For comparison, if the particulate mixture is the same, except that chromium is used instead of chromium carbide, the carbon will first react with the iron and chromium to form iron-carbon, chromium-carbon, and some iron-chromium. Then, a homogeneous alloy of iron, chromium and carbon will be formed in the solid-liquid phase. The time required to reach the solid-liquid phase conditions, is therefore considerably longer than in the present invention. That is, in the present invention, which uses chromium carbide, the carbon powder cannot react with the carbide. The reaction therefore involves only the carbon and iron particles. Since the iron-caron alloy is formed quite rapidly, the solid-liquid phase is obtained in a relatively shorter period of time. The required sintering period is therefore considerably shorter in the present invention.

In contrast, if the particulate mixture is heated only up to the solid phase temperature, from 800°C. to 1,120°C., as in the conventional methods, the particulate mixture will be alloyed and a solid state sintered body will be formed. The voids in the sintered body in the solid state will remain, even if very high pressure is applied to the powder, so that it is impossible to obtain a product having as high a density as in the present invention.

In the present invention, the final sintering temperature is not in the solid phase temperature range, but in the solid-liquid phase temperature range. The particulate material is heated in the following manner: The particulate material is packed into a mold and it is placed in a furnace, wherein the contents are heated to a solid-liquid phase temperature. Alternatively, the particulate material may be placed into a furnace which is already within the critical temperature range.

In a second embodiment of this invention, a sintered body having a density almost as high as obtainable using molten material, can be herein attained by applying high pressures during the sintering process. Even without the use of high pressures, however, a sintered alloy having a density of higher than that obtainable by conventional techniques can be obtained.

When using the present technique, it has been found that, in general, the higher the sintering temperature, the higher will be the density obtained. As the temperature is raised, however, the sintering operation becomes more complicated and accordingly, it is preferable to use a sintering temperature in the lower portion of the solid-liquid phase temperature range.

The particulate mixture used herein contains iron powder and carbon powder, such as powdered graphite, or a powder of an iron-carbon alloy, such as cast iron. In the latter case, the iron and carbon are preformed as an alloy, so that the sintering operation can be carried out in a shorter period of time.

Suitable powdered metallic carbides which can be used include tungsten carbide, molybdenum carbide, manganese carbide, chromium carbide, titanium carbide, vanadium carbide, niobium carbide, tantalum carbide, boron carbide or the like, or a mixture thereof depending upon the intended end composition of the alloy.

The particulate material may be sintered in a mold made of ceramic, for example, alumina, which will not react with the alloy and which is capable of enduring the sintering temperatures. The mold may be of the type used for forming sintered body materials, such as planar materials and rod materials, or may have a molding surface which is similar to the outer surface of the sintered products.

Also, by using the techniques of this invention, a previously sintered, void-containing, iron-base alloy can be re-sintered to the solid-liquid phase temperature range and the density will be markedly improved.

Having now generally described the invention, a further understanding can be attained by reference to certain specific Examples which are provided herein for purposes of illustration only and are not intended to be limiting in any manner unless otherwise specified.

EXAMPLE 1

In this Example, a sintered alloy of Fe-1.5% Cr-3.9% C, is produced. Samples 1 and 2, as shown in Table I, were used as the particulate material. The particulate material was packed into a container made of alumina and heated in an electric furnace made of graphite. A predetermined pressure of **10.3** 10.3Kg/cm^2 was applied to the contents of each container by putting an alumina punch and an iron weight onto said material. This container was then placed into the furnace and heated to a temperature of about 600°C. The temperature of the furnace was then increased at a rate of about 45°C./minute to the sintering temperature of 1,200°C. in the solid-liquid phase temperature range. The temperature was held at this point for 5 to 30 minutes. Next, the furnace was cooled to about 1,000°C. at a rate of about 15°C./minute and the container was removed from the furnace and air-cooled. The density (g/cm^3) and the Brinell hardness (H_B) of the sintered alloys obtained are also shown in Table I, and in FIG. 2 as curves with the same marks as those of the samples of Table I. The abscissa of FIG. 2 represents sintering time in minutes and the ordinate represents density and hardness. In sample 1 of Table I, chromium carbide powder (Cr_3C_2, −200 mesh) was used as the chromium

source. In sample 2, a ferrochromium powder (Fe-63.4%Cr, −200 mesh) was used as the chromium source. In each instance, the particulate material was mixed to form the same sintered alloy composition as that of the Sample 1 for purposes of comparison with the Sample 1. Electrolytic iron powder (-100 mesh) and graphite powder (average particle size 24μ) were respectively used as the iron powder and the carbon powder sources. The density of the products was measured by Archimedes' principle (thie method was employed in the following embodiments). Hardness was measured as Brinell hardness using sintered bodies which were heated to 950°C. for 20 minutes and then oil-cooled. The solid-liquid phase temperature range in the Table shows the corresponding mixing ratio of iron and graphite (Fe-2%C), excluding chromium carbide, in Sample 1, and also shows that corresponding mixing ratio (Fe-1 5% Cr-3.9% C) of particulate material in Sample 2.

TABLE I

Samples	Mixing ratio of particulate material	(Weight %)	Solid-liquid phase temperature range (°C.)	Sintering time (minutes)	Density (g/cm³)	Hardness of (H_B)
1	Iron	81.1%	1,149	5	7.1	420
	Graphite	1.6%	∫	10	7.4	560
	Chromium carbide	17.3%	1,390	30	7.4	610
2	Iron	72.5%	1,150	10	6.5	290
	Graphite	3.9%	∫	13	6.8	360
	Ferrochromium	23.6%	1,200	30	7.2	480

In this case, the theoretical density of the sintered alloy was about 7.5 g/cm³. When a particulate material of the same composition as that of Sample 1 was heated for 30 minutes at the solid phase temperature, 1,100°C. under a pressure of 10.3 kg/cm², the density of sintered alloy was 3.8 g/cm³, and its hardness could not be measured because the sintered alloy was very porous and brittle.

The density of Sample 1, sintered in the solid phase condition by conventional methods, reaches only 50 percent of the theoretical density, even if it is heated for as long as 30 minutes. According to the method of the present invention, the density reaches about 95 percent of the theoretical density by solid-liquid phase sintering for only 5 minutes and it reaches almost equal to the theoretical density by solid-liquid phase sintering for 10 minutes. With respect to Sample 2, which does not include chromium carbide, the density reached 87 percent of the theoretical density by solid-liquid phase sintering for 10 minutes, and reached 96 percent of the theoretical density by solid-liquid phase sintering for 30 minutes. In both cases of Sample 2, relatively high density can be obtained as compared with the conventional solid phase sintering method. However, the density is lower than that of Sample 1. Therefore, it is considered that high density and high hardness sintered alloys can be obtained within a short period of time by sintering Sample 1 including chromium carbide in solid-liquid phase temperature range.

EXAMPLE 2

In this example, a sintered alloy of Fe-10% Mo-2.4%C, is produced using Samples 3 and 4 as shown in Table II. Each material was sintered for 6 to 30 minutes at a temperature of 1,200°C. and a pressure of 4.4 kg/cm². The density and the Brinell hardness of the sintered alloys obtained are shown in Table II and also in FIG. 3 with respect to sintering time as curves with the same marks as those of the samples in Table II.

In Sample 3 of Table II, the molybdenum carbide powder (Mo_2C, the particle size was about 5μ) was employed as the molybdenum source. In Sample 4, a ferromolybdenum powder (Fe-62.5% Mo,−100 mesh) was employed as the molybdenum source. The particulate material was mixed so as to have the same sintered alloy composition as that of Sample 3 for purposes of comparison. The sintered alloys were heated for 20 minutes at a temperature of 1,000°C. and were water-cooled. The Brinell hardness was measured. The solid-liquid phase temperature range in Table II shows the corresponding mixing ratio of iron and graphite (Fe-2%C), excluding molybdenum carbide from the mixture, in the Sample 3, and also the corresponding mixing ratio (F3-10% Mo-2.4%C) of particulate material in Sample 4.

TABLE II

Samples	Mixing ratio of particulate material	(Weight %)	Solid-liquid phase temperature range (°C.)	Sintering time (minutes)	Density (g/cm³)	Hardness of (H_B)
3	Iron	87.5%	1,149	6	7.2	450
	Graphite	1.8%	∫	10	7.6	600
	Molybdenum carbide	10.7%	1,390	30	7.8	670
4	Iron	81.6%	1,080	10	6.6	420
	Graphite	2.4%	∫	14	6.8	440
	Ferro-molybdenum	16.0%	1,330	30	7.2	550

TABLE III

Samples	Mixing ratio of particulate material	(Weight %)	Solid-liquid phase temperature range (°C.)	Sintering time (minutes)	Density (g/cm³)	Hardness of (H_R)
5	Iron	77.1%	1,149	10	8.8	640
	Graphite	1.6%	∫	20	8.9	650
	Tungsten carbide	21.3%	1,390	30	8.9	650
6	Iron	72.5%	1,080	10	8.0	500
	Graphite	2.9%	∫	20	8.2	530
	Ferrotungsten	24.6%	1,240	30	8.3	570

The theoretical density of the sintered alloy is about 8 g/cm³. When particulate material having the same composition as Sample 3 was sintered for 30 minutes at a temperature of 1,100°C., i.e., in solid phase under a pressure of 4.4 kg/cm² according to conventional methods, the density of the sintered alloy obtained was 4.2 g/cm³, but its hardness could not be measured because the product was too porous and brittle.

The density of Sample 3 sintered in the solid phase temperature range by conventional methods reached only 52 percent of the theoretical density, even if it was heated for as long as 30 minutes. According to the method of the present invention, however, the density of Sample 3 reached about 90 percent of the theoretical density by solid-.iquid phase sintering for only 6 minutes, and reached 95 percent by solid-liquid phase after sintering for 10 minutes. It reached almost equal to theoretical density by solid-liquid phase sintering for 30 minutes. When Sample 4 which contained ferro molybdenum instead of molybdenum carbide was heated for 10 minutes, the density reached relatively higher values than that obtained by sintering in the solid phase temperature range. Even if it were heated for 30 minutes, however, the density remained the same as if Sample 3 were heated for 6 minutes. Therefore, it is considered that high density and high hardness sintered alloys can be obtained within a short period of time by sintering the Sample 3 containing molybdenum carbide within the solid-liquid phase temperature range.

EXAMPLE 3

In this example, sintered alloys of Fe-20%¶ -2.9%C, were produced. Samples 5 and 6 are shown in Table III. These materials were sintered for 10 to 30 minutes at a temperature of 1,200°C. and a pressure of 4.4 kg/cm² as in Example 1. The density and the Brinell hardness of the sintered bodies obtained are shown in Table III and also in FIG. 4 with respect to the sintering temperature as curves with the same marks as those of the samples in Table III.

In Sample 5, tungsten carbide powder (WC, 250 to 325 mesh) was used as the tungsten source, and in Sample 6, ferro-tungsten powder (Fe-81.4%W,—100 mesh) was used as the tungsten source. The particulate material was mixed so that each sintered alloy will have the same composition as Sample 5 for purposes of comparison. The sintered alloys were re-heated for 20 minutes at a temperature of 1,000°C. and oil-cooled, and then the Brinell hardness was measured. The solid-liquid phase temperature range shows that the mixing ratio of iron and graphite was (Fe-2%C), excluding tungsten carbide, from the mixture in sample 5, and was (Fe-20%W—2.9%C) of particulate material in Sample 6.

The theoretical density of the sintered alloy is about 10 g/cm³. When the Sample 5 was sintered for 30 minutes at the solid-phase temperature of 1,100°C. under a pressure of 4.4 kg/cm² according to conventional methods, its density was 3.9 g/cm³, but its hardness could not be measured because of the porous and brittle nature of the product.

The density of Sample 5, when sintered at a solid-phase temperature for 30 minutes, reached only 39 percent of the theoretical density. But according to the present invention, the density reached almost 90 percent of the theoretical density by sintering for only 10 minutes in the solid-liquid phase.

When Sample 6 not including tungsten carbide is sintered in a solid-liquid phase for 10 minutes, the density becomes relatively higher than that obtainable by sintering in the solid phase. Even if it is sintered in the solid-liquid phase for 30 minutes, the density will remain at 83 percent of the theoretical density. Therefore, according to the present invention, it is apparent that high density and high hardness sintered alloys can be obtained by sintering Sample 5 including tungsten carbide in the solid-liquid phase.

Having now fully described the invention, it will be apparent to one of ordinary skill in the art that many changes and modifications can be made thereto without departing from the spirit of scope of the invention as set forth herein.

What is claimed and intended to be covered by Letters Patent is:

1. A method for producing a high density, high hardness sintered iron-base alloy which comprises:

heating a mixture of particulate material selected from the group consisting of mixed particles of iron, carbon and metallic-carbide particles, and mixed particles of an iron-carbon alloy particles and metallic particles, said metallic carbide being selected from the group consisting of tungsten carbide, molybdenum carbide, manganese carbide, chromium carbide, titanium carbide, vanadium carbide, niobium carbide, tantalum carbide, boron carbide, and mixtures thereof, at a temperature within the range of the solid-liquid phase of the resulting alloy,

said sintering temperature being lower than the melting points of any of said starting particles,

maintaining the sintering temperature for a period sufficient to cause sintering, and

cooling said sintered iron base alloy.

2. The method of claim **1**, wherein pressure is applied to said particulate material during sintering.

3. The method of claim **1**, wherein the particulate material is sintered in a suitable mold, and the sintered product is subsequently removed from said mold.

4. The method of claim **3**, wherein said mold is formed from a ceramic material.

5. The method of claim **1**, wherein said carbon is in the form of graphite.

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