

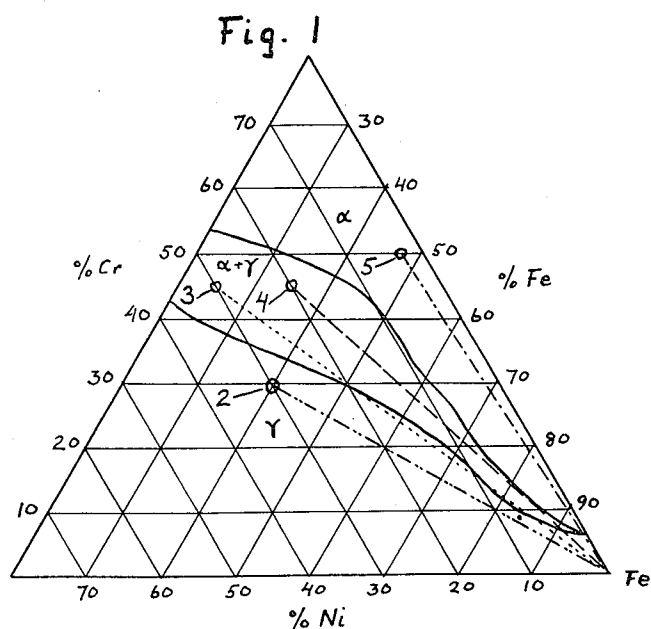
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METHOD FOR THE POWDER METALLURGICAL
MANUFACTURE OF CHROMIUM ALLOYS

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2 Sheets-Sheet 1



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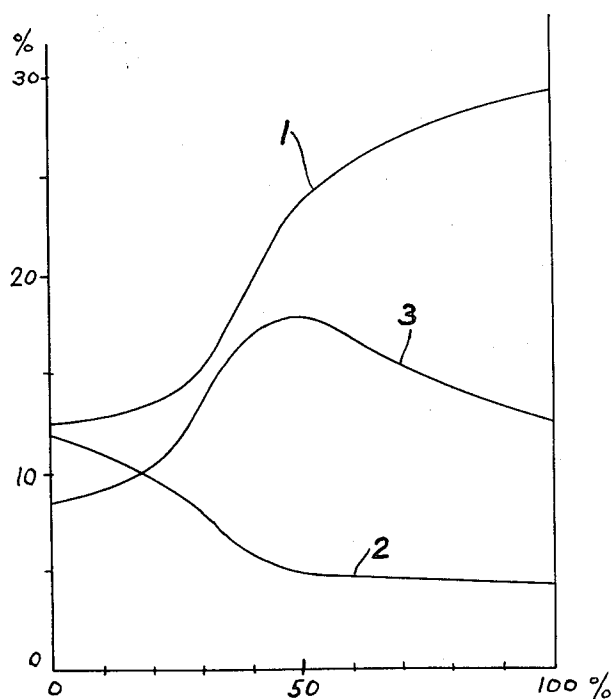
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Fig. 2



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METHOD FOR THE POWDER METALLURGICAL MANUFACTURE OF CHROMIUM ALLOYS

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The present invention relates to the production of corrosion resistant metal bodies by pressing metal powder into compacts and sintering them.

The powder-metallurgical technique has become more and more important during the last decade. In many cases, for instance in the production of hard metals and pure high melting metals, the powder metallurgical method has proved to be the only practicable way to carry out a large scale economical manufacture. Powder metallurgy has also gained ground from the conventional steel-making processes as a number of parts of different steels and even pure soft iron nowadays are produced, to a great extent, by the pressing and sintering of powder and powder mixtures. A certain specified alloy may thus be prepared according to a large number of various recipes. The powders may consist of pure metals or metalloids, of alloys or even of finely disintegrated material of exactly the same composition as that of the finished body. Instead of metal powders, metal compounds such as oxides, hydrides and different salts may be used.

So-called stainless steel grades and high-alloy compositions related thereto have hitherto been manufactured by powder metallurgical methods to a limited extent only, in spite of the fact that such a production method would be particularly advantageous for these materials. Many high alloyed materials are difficult and expensive to roll, forge and form in the hot as well as in the cold. Furthermore, usually they are difficult to machine by means of cutting tools, e.g. turning, milling and drilling tools.

The main reason for the restricted application of powder metallurgy in these cases is the fact that the bodies manufactured according to powder metallurgical methods hitherto known were not as resistant to corrosion as bodies manufactured in accordance with conventional steel-making methods. For satisfactory corrosion resistance there is required, on the one hand, physical homogeneity (as low a grade of porosity as possible), and, on the other hand, chemical homogeneity. Up till now, the position in most cases has been that it is possible to realize only one of these conditions by a given method, provided moderate compacting pressures, sintering temperatures and sintering times are used.

In many cases the pressing and sintering of a mixture of powders of the component metals may give a quite good physical homogeneity, for instance, if the major part of the powder mixture consists of a soft powder. However, the chemical homogeneity will not be satisfactory even if the bodies are treated for a long time at high temperature. This is due to the comparatively low diffusion rates of such metals as chromium, nickel and molybdenum. The diffusion of chromium is obstructed by the so-called passive films, of which more will be said below.

Chemical homogeneity will of course be obtained by the pressing and sintering of a powder, every particle of which has the same composition as the desired body in its finished state. However, such powders most often

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have poor compressibility, due, inter alia, to the fact that alloyed metal particles ordinarily are harder and less deformable than pure metal particles. The finished body will thus have a relatively high porosity even if very high loads are applied during the pressing.

The passive film, which is formed on the surface of alloy particles containing more than about 10–12% chromium, renders the growing together of the particles difficult. This drawback can be overcome in part by intermixing low melting fluxing agents such as ferrobore, but such additions decrease the corrosion resistance and the mechanical properties (strength and ductility) of the finished body.

All of the methods hitherto used suffer from an essential drawback in that the powders are rather expensive.

The present invention relates to a solution of the problem of producing by means of powder metallurgical methods alloys containing at least 10% chromium, and having good chemical as well as physical homogeneity. The method according to the invention comprises mixing a soft powder containing at least one of the elements constituting the finished product with an alloy powder, the structure of which consists of at least 25% of at least one phase of the group consisting of the sigma, mu, xi and chi phases, pressing the powder mixture to form a body and sintering said body at a temperature below the melting point of the pulverulent components of the mixture.

In spite of the fact that great atomic movements must take place during the diffusion and in spite of the fact that no molten phase is formed, it is possible according to the present invention, using comparatively very short sintering times, to produce sintered bodies having a good chemical homogeneity and a very high density, i.e., only a very small porosity.

Some of these phases have been discovered only recently and the nomenclature has not been definitely established but it is known that the mu, xi and chi phases are related to the sigma phase and have similar crystal structures. Reference is in this respect made to Hume-Rothery: The Structure of Metals and Alloys.

The sigma phase has hitherto won a reputation only as an undesirable and injurious structural component of so-called stainless and related grades of steel. The sigma phase is an intermetallic compound which can be formed by interalloying two or more of the metals Fe, Cr, Ni, Co, V, Mn, Mo, W and others. Many of these intermetallic compounds have only quite lately been discovered. Tables 1–3 exemplify some of these compounds. Among other things they are characterized by a crystal structure wherein the atoms are arranged in very dense lattices.

Below will be given, firstly, the recently published compositional limits for the existence of the pure sigma and related phases for a number of binary (Table 1) and ternary (Table 2) alloys, and secondly (Table 3) a number of alloys which according to our own practical tests have proved to be useful in accordance with the invention.

In some important cases (e.g. acid resisting

Cr—Ni—Mo

steels) it is feasible to obtain a structure (of the alloy powder) with a sufficient proportion of sigma phase without incorporating therein alloying elements other than Cr, Ni and Mo. In other cases, however, it may be necessary, in order to obtain the desired proportion of sigma phase, to add elements which would not be necessary in view of the corrosion resistance properties of the finished steel but which in that respect are harmless. We have found that the alloy powder may contain besides iron and chromium one or more of the following

elements: Ni, Mo, W, Cu, Co, Mn, Ti, V, Nb, Ta, Si, Zr, Al, P, N and C.

Table 1

System	Decomposition temperature	Range of stability
V-Ni-----	>1,200° C-----	51-63% V.
V-Co-----	>1,200° C-----	41-51% V.
V-Fe-----	>1,075° C-----	37-51% V.
V-Mn-----	>1,000° C-----	13-23% V.
Cr-Fe-----	Approx. >800° C-----	41-47% Cr.
Cr-Co-----	>1,200° C-----	55-59% Cr.
Cr-Mn-----	>1,000° C-----	16-23% Cr.
Mo-Fe-----	<1,180° C. Approx.	63% Mo.
Mo-Co-----	probably 1,200° C. Approx.	75% Mo.
Mo-Mn-----	only stable at high temperatures.	not established.
W-Co-----		
W-Fe-----		

The alloys of the above table are of sigma type. Alloys containing phases of a closely related type and alloys containing mixtures of such phases and sigma phase are formed by the additional alloying of Nb and/or Ta.

Table 2

System	Range of stability	Type of brittle phase
Cr-Co-Ni-----	Cr: 55-59%----- Co: 18-45%----- Ni: 0-22%-----	sigma.
Cr-Co-Fe-----	Cr: 49-59%----- Co: 32-45%----- Fe: 0-17%-----	
Cr-Co-Mo-----	Cr: 25-59%----- Co: 40-46%----- Mo: 0-30%-----	
Cr-Ni-Mo-----	Cr: 22-48%----- Ni: 22-31%----- Mo: 24-48%-----	sigma.
Fe-Co-Mo-----	Fe: 0-47%----- Co: 0-45%----- Mo: 52-61%-----	
Fe-Ni-Mo-----	Fe: 23-47%----- Ni: 0-20%----- Mo: 52-61%-----	
Ni-Co-Mo-----	Ni: 0-24%----- Co: 17-46%----- Mo: 53-62%-----	mu.

Table 3

	Per- cent Cr	Per- cent Ni	Per- cent Mo	Per- cent Cu	Per- cent Mn	Per- cent Si	Per- cent Ti	Per- cent Nb
(1)-----	51	7				1.5		
(2)-----	45	7						
(3)-----	47	12						
(4)-----	47	19	4					
(5)-----	43	19	5	4				
(6)-----	43	21					2	4
(7)-----	44	18	6	8				
(8)-----	44	4	5		30			

All these alloys contain sigma phase. The alloys (4), (5) and (7) probably also contain xi phase. The carbon content is low. In all cases the remainder consists of iron with the usual impurities.

It is not yet quite clear how the sigma and related phases effect their favourable influence, but probably the following factors are involved:

(1) The breaking of passive films on the surface of the particles due to the increase of volume when the sigma and related phases transform to alpha phase.

(2) The high reactivity of the particles during and after the phase transformation (the Hedvall effect).

(3) The increased rate of diffusion due to the increase of the interatomic distance which results from the lattice transformation.

(4) The gradual increase in volume of the soft powder particles as the diffusion of chromium proceeds into them, as described below.

As will be shown below—and this is quite unexpected—the very porous compacts made of brittle powder of sigma and related phase alloys when heated for a short

time far below their melting point in a hydrogen atmosphere, sinter to dense bodies. This feature constitutes the basis of this invention. As will also be shown below, this considerable sinterability of sigma and related phase alloys is also effective if another powder is admixed with the sigma and related phase alloy powder. A powder mixture of e.g. 1 part sigma and related phase alloy and 1 part iron after a short sintering period consists of a skeleton of alpha phase (formerly sigma and related phases) in which the particles of iron (gamma phase) are embedded. As would be expected such a sinter body has a somewhat higher porosity. The contact between the iron and the alloy-skeleton is, however, very effective. The passive film is broken and thus the diffusion conditions are very good. As diffusion proceeds the iron particles become enriched with chromium and gradually transform from gamma to alpha phase. This transformation is accompanied by a volume increase which, taking place in the cavities of a stiff skeleton, leads to a gradual compression and diminution of the still present pores.

The essential features of the invention having now been described, a number of details will be given, the incorporation of which has proved to improve the sintering results.

As indicated above the powder admixed with the alloy (sigma and related phase containing) powder should be soft. The reason is that a sufficiently high so-called green density and green strength (density and strength of pressed, not sintered, compacts) thus obtained. A high green density results in less shrinkage after sintering which also is an advantage.

The powder mixture which is to be pressed and sintered, may also contain other component powders, e.g. a powder which does not contain sigma or related phase and which consists of one or more alloying elements. In order to facilitate diffusion, however, the powder mixture should contain only a few component powders and preferably only two. Therefore, the soft powder as well as the alloy powder should be uniform, and the alloy powder should contain all the alloying elements and possibly also part of the soft powder metal.

The green density is favourably influenced by a suitable distribution of the grain size of the powders. From the point of view of diffusion it is desirable that the powders have substantially the same screen analysis. All powders should be fine-grained, the diffusion then requiring less time. It has been found suitable to use a particle size of <0.074 mm. (200 mesh) and preferably <0.044 mm. (325 mesh).

The soft powder should be as ductile as possible. The chemical composition should be proportioned so that the mass ratio of soft powder to alloy powder is between 2 to 1 and 1 to 2. From the point of view of diffusion it is desirable that said ratio be about 1 to 1, so that particles of both powders will with the greatest probability find themselves next to each other in the final mixture, whereby the diffusion distance will be the shortest possible. A high proportion of the hard alloy powder in the powder mixture is harmful as it accelerates the wearing of the pressing tools. A high proportion of the soft powder component on the other hand results in an increased porosity of the body after sintering.

The soft powder most frequently used according to this invention is pure iron, e.g. electrolytic iron. Other examples are low alloyed iron, pure nickel, pure cobalt or some binary or ternary alloys of said metals.

The alloy powder should contain all the sluggish diffusing elements to be contained in the finished sintered steel. It should be uniform, i.e. each particle of the powder should have the same chemical composition. As the soft powder preferably consists of a single metal the alloy powder should thus contain all the other elements.

In principle, the use of alloy powders is not new in powder metallurgy. Thus it is known to use so-called master alloys, especially when introducing into a sintered

compact volatile elements such as sulphur, or elements which easily form gaseous compounds, such as carbon. Ferrochromium, ferro-molybdenum and other ferro-alloys which are added to powder mixtures when producing low alloyed steel are also examples of such master alloys. In order to facilitate diffusion according to the invention the idea of master alloying should be carried out as far as possible keeping in mind that the master alloy must also have a defined metallographic structure containing at least 25 percent of sigma and/or related phase.

The alloy powder can be selected with such a composition that the sigma or related phase is transformed to alpha phase merely by the temperature being raised above a certain limit or threshold value which is found at different levels for the various alloys. Other alloys which are suitable for performing the method according to the invention contain a sigma or related phase which is stable to very high temperatures, in some cases up to the melting point, and the phase transformation in these cases is brought about by the diffusion of the soft metal into the particles of the alloy, whereby the critical chemical composition is successively attained and the phase transformation takes place. In such a case a very high density may be obtained, but longer time is required for complete diffusion.

Of course, the diffusion takes place at a higher rate at the beginning and gradually slows down as the concentration gradient gets smaller. A complete equalisation of analysis will therefore necessitate a very long period of time. This disadvantage can be neutralized according to the invention in a simple way by employing a minor excess of one or more alloying elements, the content of which must not, in any part of the final sintered body, be below a certain limiting value, which is decisive for the corrosion resistance. When producing a pressed and sintered body of e.g. 18/8 composition the proportion of alloy powder to soft metal powder (iron powder) is so chosen that it approximately corresponds to the composition 20% Cr and 8% Ni. Even if the diffusion of chromium is not complete, those parts of the structure which have not entirely diffused will in this case have such a high content of chromium that they will possess sufficient resistance against corrosion.

The influence of the structure of the alloy powder upon the result of the sintering and diffusion will be evident from the experimental results below (see also the ternary phase diagram in Figure 1). In all tests powders were used having a particle size of <0.044 mm. (325 mesh). Briquets were pressed (compacting pressure 7.5 metric tons/cm.²) from the various powder mixtures (1 part of soft powder+1 part of alloy powder). The sintering was performed in pure hydrogen for two hours at 1310 C.

(1) Merely soft powder (electrolytic iron). Specific gravity after sintering 6.96. Porosity 11.8%.

(2) Soft powder according to Example 1+alloy powder of composition 30% Cr, 30% Ni and the rest Fe (point 2 in the diagram). The structure of the alloy powder is gamma. Specific gravity after sintering 6.95. Porosity 13.1%. Corrosion resistance in boiling 10% HNO₃ (48 hrs.) in comparison with cast alloy of the same composition: Loss in weight in g./m.²h.—Sintered metal 0.5; casting 0.00.

(3) Soft powder according to Example 1+alloy powder of composition 45% Cr, 30% Ni and the rest Fe (point 3 in the diagram). The structure of the alloy powder is alpha+gamma. Specific gravity after sintering 6.10. Porosity 22.6%. Corrosion resistance in boiling 65% HNO₃ (48 hrs.) in comparison with casting alloy of the same composition: Loss in weight in g./m.²h.—Sintered metal 66; casting 0.1.

(4) Soft powder according to Example 1+alloy powder (in accordance with the invention) of composition 50% Cr, 3% Ni and the rest Fe (point 5 in the diagram).

The structure of the alloy powder is sigma and/or related phase. Specific gravity after sintering 7.38. Porosity 3.7%. Corrosion resistance in boiling 65% HNO₃ (48 hrs.) in comparison with casting alloy of the same composition: Loss in weight in g./m.²h.—Sintered metal 0.9; casting 0.6.

(5) Soft powder according to Example 1+alloy powder (in accordance with the invention) of composition 45% Cr, 20% Ni, 5% Mo and the rest Fe (point 4 in the diagram). The structure of the alloy powder is sigma and/or related phase+gamma. Specific gravity after sintering 7.51. Porosity 4.5%. Corrosion resistance in boiling 65% HNO₃ (48 hrs.) in comparison with casting alloy of the same composition: Loss in weight in g./m.²h.—Sintered metal 1.1; casting 1.1.

(6) Soft powder according to Example 1+ferrochromium powder+carbonyl nickel powder+ferromolybdenum powder. The composition of the sintered body is the same as that of the body described in Example 5. Specific gravity after sintering 6.88. Porosity 11.7%. Corrosion resistance in boiling 65% HNO₃ (48 hrs.) in comparison with a casting alloy having the same composition: Loss in weight in g./m.²h.—Sintered metal 5.4; casting 1.1.

These experimental results clearly show that only the sigma and/or related phase containing powder mixtures yield sinter bodies of the density and corrosion resistance required.

In another experiment bodies consisting merely of the pure alloy powders used in the above examples were pressed and sintered. The pressing and sintering conditions were the same as in the above examples. The specific gravity of the bodies was determined before and after the sintering.

(7) Alloy powder having the composition described in Example 2, i.e. containing 30% Cr, 30% Ni, the remainder being iron. The structure is gamma. Specific gravity: before sintering 5.9; after sintering 6.6.

(8) Alloy powder having the composition described in Example 3, i.e. containing 45% Cr, 30% Ni, the remainder being iron. The structure is alpha+gamma. Specific gravity: before sintering 5.8; after sintering 6.5.

(9) Alloy powder having the composition described in Example 4, i.e. containing 50% Cr, 3% Ni, the remainder being iron. The structure is sigma or related phase. Specific gravity: before sintering 5.3; after sintering 7.2.

(10) Alloy powder having the composition described in Example 5, i.e. containing 45% Cr, 20% Ni, 5% Mo, the remainder being iron. The structure is sigma or related phase+gamma. Specific gravity: before sintering 5.3; after sintering 7.6.

Obviously, the sigma or related phase containing powders have sintered to very dense bodies, in spite of the fact that it has not been possible to compress said powders, owing to their hardness, to a green density higher than 5.3. The softer powders, which do not contain sigma or related phase, may be pressed to a higher green density of 5.8–5.9, but this is increased very insignificantly during sintering.

In Example 10 the specific gravity of the body being sintered was also determined as a function of time. The following results were obtained.

Sintering time, in minutes, at full sintering temperature	Specific gravity
15	7.38
30	7.43
45	7.46
60	7.51
90	7.57
120	7.60

The table shows that sintering occurs very rapidly. Thus, a sintering time of 15 minutes gives a specific gravity of 7.38. As a contrast Example 8 may be mentioned, in

which a powder is sintered having approximately the same content of alloying elements but containing no sigma or related phase. After two hours sintering the powder which is free of sigma and related phases has a specific gravity which is only 6.5.

Figure 2 shows the results of a series of tests in which an alloy powder as described in Example 5, i.e. containing 45% Cr, 20% Ni, 5% Mo, the remainder being iron, was mixed with electrolytic iron powder in different ratios, and the mixtures then pressed and sintered under the same conditions as described in the above examples. Curves 1 and 2 show the pore volume (along the ordinate) as function of the proportion (along the abscissa) of alloy powder in the powder mixture, curve 1 referring to the bodies before sintering (green), and curve 2 after sintering. Curve 3 illustrates the decrease of porosity during sintering as a function of the proportion of alloy powder in the powder mixture. Curve 3 shows that the alloy powder has its maximum porosity-decreasing ability when the ratio base powder to alloying powder is about 1 to 1.

Most of the stainless sinter powders which at present exist on the market are produced by means of atomisation and will thus consist of particles all of which have the same composition as the finished stainless sinter body. Below (Table 4) a few comparative data are presented of sintered briquets produced from such a powder (A), from a powder mixture as described in Example 5 above (B) (in accordance with the invention), and finally, of rolled stainless steel (C) produced by conventional melting.

Table 4

	B	A	C
Compacting pressure tons/cm. ²	5	12	
Sintering temperature, ° C	1,310	1,350	
Sintering time, hrs.	3	6	
Specific gravity of sintered body	7.55	6.98	7.85
Composition:			
Percent C	0.02	0.06	0.06
Percent Cr	21.2	18.5	18.7
Percent Ni	8.5	10.5	12.5
Percent Mo	2.1	2.2	2.4
Loss in weight in g./m. ² h. after boiling in 65% HNO ₃ for 48 hrs. (acc. to ASTM)	0.3	68	0.3
Yield strength, kgs./mm. ²	58	53	55
Elongation, percent	25	30	40
Hardness (Vickers)	200	190	180

The table shows the sintered steel produced in accordance with the invention to be of equal merit, from the standpoint of corrosion resistance, with rolled stainless steel produced in the conventional way. This is, however, not the case with material produced from atomized powder, the corrosion resistance of which is very poor. Both types of sintered steel have mechanical properties which are somewhat inferior to those of rolled material but approximately equal to those of stainless castings.

What I claim is:

1. A method for the powder metallurgical manufacture of alloys which comprises forming a mixture the major part of which consists of two powders one of which is a ductile metal powder and consists essentially of at least one of the metals of the group consisting of iron, cobalt and nickel and the other of which is an alloy

powder the structure of which consists of at least 25% of at least one phase of the group consisting of the sigma, mu, xi and chi phases, said powder mixture containing at least 10% of chromium, pressing said mixture to form a coherent body and heating said body at a temperature below the melting points of said two powders but at a temperature and for a time sufficient to cause a diffusion reaction between said powders to form a substantially chemically homogeneous alloy which is substantially free of said phase and to cause sintering together of said powders, the ratio of said ductile metal powder to said alloy powder in said mixture being within the range from 2 to 1 to 1 to 2.

2. A method as claimed in claim 1, in which all the particles of the ductile powder have the same composition.

3. A method as claimed in claim 1 in which all the particles of the alloy powder have the same composition.

4. A method as claimed in claim 1 in which the alloy powder contains the whole amount of the alloying elements to be contained in the finished body.

5. A method as claimed in claim 1, in which the ductile powder consists of one metal.

6. A method as claimed in claim 5, in which the ductile powder consists of substantially pure iron.

7. A method as claimed in claim 5, in which the ductile powder consists of substantially pure nickel.

8. A method as claimed in claim 1, in which the ductile powder and the alloy powder have such compositions that the finished sintered body has the composition of a stainless chromium steel.

9. A method as claimed in claim 7, in which the alloying powder has such a composition that the finished sintered body contains about 13% chromium and about 80% nickel, the remainder being iron.

10. A method as claimed in claim 1 in which the alloy powder contains about 45% chromium, 20% nickel and 5% molybdenum, the remainder being iron.

11. A method as claimed in claim 1 in which the ductile powder and the alloy powder each has a grain size of less than 0.074 millimeter.

12. A method as claimed in claim 1 in which the alloy powder consists of substantially pure sigma phase.

13. A method as claimed in claim 1 in which the ductile powder and the alloy powder each has a grain size of less than 0.044 millimeter.

14. A method as claimed in claim 1 in which the ratio of ductile powder to alloy powder is between 2 to 1 and 1 to 2.

15. A method as claimed in claim 1 in which the alloy powder contains less than 0.10% carbon.

16. A method as claimed in claim 1 in which the ratio of ductile powder to alloy powder is about 1 to 1.

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