United States Patent Office 3,451,809
Patented June 24, 1969

3,451,809

METHOD OF SINTERING MARAGING STEEL WITH BORON ADDITIONS

Rasipuram Subramanya Kalyana Raman, Madras, India, and Victor Allen Tracey, Solihull, England, assignors to The International Nickel Company, Inc., New York, N.Y., a corporation of Delaware

No Drawing. Filed Mar. 8, 1968, Ser. No. 711,482
Int. Cl. B22f 3/16; C22c 39/20, 39/54
U.S. Cl. 75—205 3 Claims

ABSTRACT OF THE DISCLOSURE

A mixture of finely divided powders for compaction and sintering to form components of maraging steel composition contains from 0.02% to 0.20%, by weight, of boron. The boron functions to reduce linear shrinkage during the sintering operation.

The invention is directed to a novel composition for the constituent powders for producing maragining steel components by powder metallurgy techniques; compacts of the constituent powders being characterized by great dimensional stability during the sintering operation.

The maragining steels have been the subject of rather intense interest and extensive development during recent years. The term "maraging" is derived from the circumstance that the final strength of these steels is determined by the development of martensite upon cooling from the austenite phase, and subsequent age hardening of the martensite.

A wide range of compositions are known which are capable of undergoing "maragining" processes. Thus, various compositions are disclosed in Bieber U.S. Patent No. 3,093,518, Decker et al. U.S. Patent No. 3,093,519, Sadowski et al. U.S. Patent No. 3,132,937, Decker et al. U.S. Patent No. 3,132,938, Floreen et al. U.S. Patent No. 3,166,406, etc. These patents disclose compositions wherein the matrix includes the elements nickel and iron and at least one of the elements cobalt, molybdenum, chromium, titanium and aluminum, as well as other elements.

It is clearly desirable to produce articles and components of maragining steels by the well known powder metallurgy processes in which a powder mixture of the desired composition is compacted and thereafter sintered. Machining and other finishing costs can be minimized by such processing and, thus, economical use of materials is effected.

One of the major problems relating to the manufacture of maragining steel products is the control of the dimension of the compacts during sintering, for it is found that during sintering, compacts of maragining steels sustain substantial shrinkage. Linear shrinkage on sintering may amount to as much as 3% or more in the maraging steels.

It has now been discovered that the inclusion of a small amount of a special agent in a maraging steel powder mixture reduces shrinkage of maragining steel powder metal compacts.

It is an object of this invention to provide means for reducing shrinkage during sintering of maraging steel powder metal compacts.

Other objects and advantages of the invention will become apparent from the following description.

In accordance with the invention, a body of maraging steel is formed by sintering a compact, the constituent powders of which include, by weight, from 0.02% to 0.20 boron.

A preferred range of boron additions to the maraging steel constituent powders, within the broader range defined above, is, by weight, from 0.05% to 0.15%. It should be understood that the boron addition of this invention may be made to the constituent powders of a broad range of maraging steels. Such maraging steels may contain, by weight, from 8% to 27% nickel, e.g. from 10% to 20% nickel, up to 18% chromium, e.g. from 2% to 8% or from 8% to 14%, and at least one ageing element selected from the group consisting of up to 30% cobalt, e.g. 1% to 20% cobalt, up to 16% molybdenum, e.g. from 2% to 15% molybdenum, up to 6% copper, e.g. from 1% to 4% copper, up to 3% titanium, e.g. from 0.05% to 2% titanium, up to 3% aluminum, e.g. from 0.05% to 1.5% aluminum, up to 5% manganese, e.g. from 0.05% to 2% manganese, up to 3% silicon, e.g. from 0.2% to 2.5% silicon, and up to 0.1% carbon, e.g. up to 0.03% carbon, and the balance essentially iron.

Elements which may be present as auxiliary hardeners or for other purposes in the alloys of this invention include, in a total amount of up to 7%, by weight, up to 1% beryllium, e.g. from 0.2% to 0.5% beryllium, up to 6% tungsten, e.g. from 1% to 3% tungsten, up to 3% in total of one or both of niobium and vanadium, and up to 1% of zirconium. Although zirconium appears to cooperate with boron in reducing shrinkage on sintering, it has an adverse effect on the impact strength of the steel and therefore preferably it is not present in amounts exceeding 0.5% and most advantageously is absent.

Small amounts of impurities such as, for example, sulfur and phosphorus, will also be present, but the total amount of such impurities should not exceed 0.05%, by weight.

One group of maraging steels to which the invention applies includes, by weight, from 10% to 20% nickel, up to 8% chromium and at least two elements in a total amount of at least 2% selected from the group consisting of up to 10% cobalt, up to 10% molybdenum, up to 3% titanium, up to 6% copper, up to 3% silicon and the balance essentially iron with small amounts of incidental impurities. A boron addition of from 0.2% to 0.2%, or preferably from 0.05% to 0.15%, is made to the constituent powders of the alloys just defined.

In a preferred composition within the broad alloy range above, a boron addition of from, by weight, 0.02% to 0.2% is made to a maraging steel comprising from 16% to 20% nickel, from 6% to 9% cobalt, from 3% to 6% molybdenum, from 0.1% to 0.8% titanium and the balance essentially iron except for small amounts of incidental impurities.

In carrying the invention into practice, the boron is mixed with the powders to be compacted and sintered in any convenient form. It may be added as finely-divided elemental boron, but in order to obtain the finest possible dispersion it is preferably added as a boron compound, for example, as finely-divided ferroboron, nickel-boron, manganese boride, nickel-chromium-boron, or zirconium boride.

The iron constituent of the powder employed in making the compacts of the invention may be in the form of a powder substantially all of which will pass through a 100 mesh British Standard Screen (B.S.S.) sieve and, more preferably, a 300 mesh B.S.S. sieve. The shrinkage on sintering depends to some extent on the size of the iron powder forming the major constituent of the compacts, and increases as the particle size decreases. The nickel constituent is preferably added in the form of fine nickel carbonyl powder (average particle size of less than 9 microns). The cobalt and molybdenum constituents are preferably added in the form of fine powders having a particle size of less than 5 microns. The copper constituent is added in the form of a fine powder that will pass

through a 300 mesh B.S.S. sieve. The titanium and silicon constituents are added in the form of finely ball-milled master alloys, such as alloys containing 76.5% nickel-23.5% titanium and 20% nickel-80% silcon, respectively, which are ground to pass through a 300 mesh B.S. sieve. The boron addition may be introduced, for example, as zirconium diboride powder having an average particle size in the range of 5 to 10 microns. Other constituents added will also be introduced in the form of fine powders.

mined, the means of several measurements being taken. The densities of the sintered compacts were also determined.

The results set forth in Table II below show the effect of the boron additions on the behavior of compacts of maraging steels on sintering. The steels identified by an asterisk in the first column were made using carbonyl iron powder, and all the others with the coarser sponge iron powder.

TABLE II

Steel No.	B addition: Added as—	B addition: Nominal (percent)	Linear shrinkage (percent)	Density (g./cm.³)	Stress (0.2% elong.), t.s.i.	Elong. on 1" (percent)
1	NiB	0	3.0	7.65		
1	NiB	0.005	2.81	7.64	49.8	3.0
1	NiB	0.01	2.50	7.61	52.0	2.6
1	NiB	0.05	1.38	7.29	51.4	1.6
1	NiB	0.10	0.85	7.15	52.5	1.0
1	NiB	0.15	1.03	7.17	55.5	0.6
1	NiB	0.20	1.34	7.31	56.9	0.7
1	ZrB_2	0.10	0.57	7.07	63.7	0.6
1	TiB_2	0.10	1.2	7.3	34	2.3
2	NiB	0	1.60	7.36		
2	NiB	0.005	1.41	7.35	45.1	4.0
2	NiB	0.01	1.26	7.32	46.9	4.5
2	NiB	0.05	1.17	7.27	48.4	4.9
2	NiB	0.10	0.24	7.07	47.5	2.0
2	NiB	0.15	0.60	7.11	51.1	2.3
2	NiB	0.20	0.92	7.19	53.6	2.4
2*	NiB	0	2.4	7.5	49	
2*	NiB	0.10	1.4	7.3	55	
3	NiB	0	2.48	7.16		
3	NiB	0.10	1.79	6.93		
4	NiB	0	3.40	6.97		
4	NiB	0.10	2.74	6.97		
5	NiB	0	0.9	7.0	25	
5	NiB	0.10	0.5	6.9	30	
5*	NiB	0	2.7	7.4	43	
5*	NiB	0.10	0.9	7.0	44	

Examples

For the purpose of illustrating the advantages of the invention, sintered body of a number of different maraging steels were made by sintering compacts of the constituent powders admixed with varying amounts of boron. The nominal compositions in weight percent of the steels to which the boron was added are set forth in Table I, the balance in each case being iron and impurities.

TABLE I

Steel No.	Percent: Ni	Co	Mo	Ti	Al	Cu	Si	Cr
1	18	7	5	0.5				
2	12		2	0.35		2		
3	12					2	2	
4	12			0.35			2	
5	12		2	0.1	0.1			5

The appropriate constituents in the form of finely-divided metallic nickel, iron, molybdenum, cobalt and copper, the iron being in the form either of sponge iron powder having a particle size less than 300 mesh B.S.S. or of carbonyl iron powder having a particle size of about 7 microns; finely-divided alloys of titanium and silicon with nickel; and the finely-divided boron carrier; were thoroughly mixed with a small proportion (0.75% by weight) of lithium stearate as lubricant by tumbling for two hours in a cone-type mixer and compacted under a pressure of 50 long tons per square inch to compacts measuring 5 x ⅝ x ⅝ inches. After heating for hour at 500° C. in dry hydrogen (dew point-40° F.) to remove the waxy lubricant, the compacts were heated to 1300° C. for 1 hour in vacuum to effect sintering. The sintered bodies of the maraging steels Nos. 1 to 5 were then heated at 480° C. for 3 hours to bring about aging. No further volume change took place during this aging treatment. The dimensions of the compacts were measured before and after sintering and the linear shrinkage thus determined, the means of several measurements being taken. The densities of the sintered compacts were also determined.

These results for Steels 1 and 2 show that the shrinkage progressively decreases as more boron is added, reaching a minimum at about 0.1% boron, and then increases again as the boron content is further increased. The decrease in shrinkage is accompanied, as would be expected, by a small decline in density of the sintered bodies. The addition of zirconium with the boron enhances the effect of the boron, but impairs the impact strength, and for the highest toughness zirconium is preferably not added. The sintered maraged steels are somewhat stronger but less ductile with increasing boron content.

The results obtained for maraging Steels 3, 4 and 5 confirm the fact that an addition of 0.10% boron substantially reduces shrinkage during sintering. Comparison of the results obtained for Steels 2 and 5 with the two different kinds of iron powder shows that while use of the very fine carbonyl iron powder increases the magnitude of the shrinkage, the beneficial effect of a boron addition is still obtained.

In order to show the unique effect of boron in reducing sintering shrinkage in maraging steel compacts, boron additions were made to the constituent powders of the three non-maraging steels set forth below in Table III:

TABLE III

Steel	Percent: Ni	Co	Mo	Cu	Ti	Si
A	5					
B	12					
C	18					

In contrast to the favorable effect of boron on the shrinkage of the maraging steels indicated in Table II, the results set forth in Table IV show that similar additions of boron to the non-maraging nickel steels A, B and C have little effect on the shrinkage, in the cases of Steels B and C the shrinkage even being slightly increased.

TABLE IV

Steel	B addition: Added as—	B addition: Nominal (percent)	Linear shrinkage (percent)	Density (g./cm.³)
A	NiB	0	1.70	6.90
A	NiB	0.003	1.57	7.04
A	NiB	0.01	1.54	7.01
A	NiB	0.05	1.48	7.02
A	NiB	0.10	1.48	7.0
A	NiB	0.15	1.43	6.99
A	NiB	0.20	1.35	6.94
B	NiB	0	1.87	7.28
B	NiB	0.1	1.95	7.23
C	NiB	0	1.95	7.33
C	NiB	0.1	2.08	7.32

The decrease in sintered density of the boron-containing compacts in Table II shows clearly that this invention is not to be confused with so-called liquid phase sintering, in which compacts contain additions in order to form substantial amounts of low-melting phases that melt during sintering and greatly increase the bond area between the particles and reduce the porosity of the compacts so that the density of the sintered bodies is increased. Although it has been proposed to add boron to steel compacts for this purpose, much larger additions are required than are made in the present process.

Although the present invention has been described in conjunction with preferred embodiments, it is to be understood that modifications and variations may be resorted to without departing from the spirit and scope of the invention as those skilled in the art will readily understand. Such modifications and variations are considered to be within the purview of scope of the specification and appended claims.

We claim:

1. In a method for making maraging steel powder metal components including the steps of compaction of the constituent powder mixture to a body of predetermined configuration, and sintering the compacted body at an elevated temperature; the improvement comprising introducing into the constituent powders, prior to the compaction step, from 0.02% to 0.20%, by weight, of boron whereby the shrinkage of the compacted body during sintering is substantially reduced.

2. A method in accordance with claim **1** wherein the boron addition amounts to from 0.05% to 0.15%, by weight.

3. The method of claim **1** wherein the constituent powders comprise, by weight, from 8% to 27% of nickel, up to 18% chromium, and at least one aging element selected from the group consisting of up to 30% cobalt, up to 16% molybdenum, up to 6% copper, up to 3% titanium, up to 3% aluminum, up to 5% manganese, up to 3% silicon, up to 0.1% carbon and, in a total amount of up to 7%, by weight, up to 1% beryllium, up to 6% tungsten, up to 3% in total of niobium and vanadium, and up to 1% of zirconium, and the balance iron except for small amounts of incidental impurities.

References Cited

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BENJAMIN R. PADGETT, *Primary Examiner.*

ARTHUR J. STEINER, *Assistant Examiner.*

U.S. Cl. X.R.

29—182.5; 75—214

PO-1050
(5/69)

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,451,809 Dated June 24, 1969

Inventor(s) Rasipuram Subramanya Kalyana Raman and Victor Allen Trac

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 1, lines 23, 27, 35, 46, 53, 55 & 61, for "maragining", read --maraging--.

Column 1, line 71, for "0.20", read --0.20%--.

Column 2, line 21, for "0.2%", read --0.02%--.

Column 2, line 40, for "0.2%" first occurrence, read --0.02%--.

Column 3, line 4, for "silcon", read --silicon--.

Column 3, line 5, for "B.S.", read --B.S.S.--.

Column 3, line 41, for "body", read --bodies--.

Column 3, line 67, for "5 x 5/8 x 5/8 inches. After heating for hour at 500°C.", read --5 x 5/8 x 5/8 inches. After heating for hour at 500°C.--.

Column 4, line 1, for "means", read --mean--.

Column 4, line 5, for "of boron additions of the behavior of compacts of", read --of the boron additions of the behavior of compacts of the--.

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NOV 10 1970

(SEAL)
Attest:

Edward M. Fletcher, Jr.
Attesting Officer

WILLIAM E. SCHUYLER, JR.
Commissioner of Patents