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[54] INTERNALLY NITRIDED STEEL POWDER AND METHOD OF MAKING

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[56] **References Cited**

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[57] **ABSTRACT**

The application describes a steel powder containing as a dispersoid therein particles of metal nitride having a free energy of formation of greater than about −21,000 cal./mole, said nitride particles being present at an interparticle spacing of less than about 2 microns. Also described is a hot pressed article produced from the powder, a method of producing the powder by internal nitridation, and a method for producing the hot pressed article.

34 Claims, No Drawings

INTERNALLY NITRIDED STEEL POWDER AND METHOD OF MAKING

The aerospace industry has brought about a substantial need for material with improved high temperature properties and capabilities. A material which can fill this need and a method for its production is described in U.S. Pat. application, Ser. No. 735,186, filed on June 7, 1968, hereinafter referred to as the copending application. It is a nitride-strengthened, stainless steel containing as a dispersoid therein particles of metal nitride having a free energy of formation of greater, i.e., more negative, than about −21,000 cal./mole. The nitrides are present at small interparticle spacings, e.g., 2 microns, which is important since the strength of the nitrided steel increases as the interparticle spacing decreases.

Although the improvement in strength realized from the steel of the copending application is very impressive with relatively thin members, i.e., members less than about 10 mils thick, it decreases as the thickness of the members increases. Thicker members generally require higher temperatures and/or longer times for diffusion of nitrogen throughout the member. Longer times are detrimental to the steel's strength as they are accompanied by larger interparticle spacings due to growth of the nitride particles. Likewise, higher temperatures are detrimental to the steel's strength since they are also accompanied by larger interparticle spacings because less nitride particles are nucleated at higher temperatures. However, the benefits of shorter times and lower temperatures must be balanced since nitriding proceeds slower at lower temperatures.

We have considerably increased the value of nitride-strengthened steel by producing thicker nitrided members, e.g., greater than 10 mils, having an increase in strength similar to that realized from relatively thin members. This was accomplished by developing internally nitrided powders with an interparticle spacing of less than 2 microns, a method for their production and a method for densifying them into thicker members substantially free of pores.

It is accordingly an object of this invention to provide a nitride-strengthened steel powder.

It is another object of this invention to provide a hot pressed member containing densified nitride-strengthened steel powder.

It is an additional object of this invention to provide a method for producing nitride-strengthened steel powder.

It is a further object of this invention to provide a method for producing a hot pressed member containing densified nitride-strengthened steel powder.

In accordance with this invention, steel powder containing a metal component capable of forming a nitride, hereinafter referred to as a nitride former, is subjected to a nitriding atmosphere at an elevated temperature so as to produce a nitride-strengthened steel powder with an interparticle nitride spacing of less than 2 microns, preferably less than 0.5 microns. The powder is thereafter hot pressed with or without the addition of dissimilar powder.

As in the copending application, various nitride formers are within the purview of the invention. The requirements of such materials are that the nitrides, i.e., the dispersoids have a sufficiently high free energy of formation to lead to the production of very small particles. Typically, such nitrides should possess a free energy of formation of greater, i.e., more negative, than about −21,000 cal./mole. They should be present in an amount sufficient to provide an interparticle spacing of less than 2 microns and preferably less than 0.5 microns, the volume percent being dependent on the interparticle spacing and being larger for a smaller interparticle spacing at a constant particle size. The nitride used should possess a very low solubility in the steel treated so as to possess a reduced tendency to coarsen at elevated temperatures such as those to which the dispersion-strengthened article will be subjected in use. Extensive evaluation has indicated that the preferred and by far most superior nitride former to be employed is titanium. Titanium has a relatively high solubility in stainless steel and its nitride has a very high free energy of formation. Other nitride formers are available, but none as good as titanium. For lower temperature applications, strengthening may be achieved by use of nitride formers such as aluminum, vanadium, and columbium. Such dispersion-strengthened materials could be used at temperatures where coarsening is not too rapid, but these materials would not have the high temperature capabilities of titanium-dispersoid strengthened steel. Still other nitride formers such as boron, zirconium, cerium, hafnium, thorium, etc., are not soluble to a high extent in steel. In the preferred embodiment in which a titanium nitride dispersoid is formed, steel containing 0.5 to 3 percent titanium is preferred. Less than about 0.5 percent titanium results in a product having satisfactory room temperature properties but the particles are such that they tend to grow at elevated temperatures and the resulting interparticle spacing might be greater than 2 microns. When more than about 3 percent titanium is present in the steel, additional improvement in properties may be obtained but such would be disproportionately less than obtainable with 0.5 to 3 percent titanium.

The nitriding atmosphere can comprise nitrogen, ammonia, mixtures of the two and mixtures of them with other compatible gases. The term compatible gases as used herein refers to nonoxidizing or inert gases such as hydrogen or argon. Ammonia is the preferred atmosphere and should be substantially free of moisture and oxygen. When using nitrogen, it is preferable to use it in a pressurized condition, i.e., at pressures above atmospheric, so as to obtain a nitriding rate comparable to that obtained from ammonia. The presence of small amounts of moisture or oxygen severely affects the nitriding rate in nitrogen.

Nitriding as described herein is both time and temperature dependent as are all diffusion processes. Temperatures generally range from 1,600° F. to just short of the melting point. However, temperatures as low as 1,400° F. can be used for finer powders, e.g., 1 mil. A preferred temperature range is 1,700°–2,200° F. This range balances the advantage of nucleating more nitride particles at lower temperatures with the accompanying disadvantage of slower nitriding times and increased dispersoid growth. Time can only be determined from the temperature and powder size, but should not be longer than that necessary for sufficient nitrogen diffusion so as to avoid unnecessary particle growth. It could be in excess of the period at which the material is exposed to the nitriding atmosphere. For example, the nitriding atmosphere could be removed with nitrogen diffusion being only a fraction of the way through the material, e.g., half way. Nitriding would then be completed by the dissolving of unstable nitrides such as chromium nitrides which release the nitrogen necessary to complete nitridation. This completion could occur at any temperature within the nitriding range and if desirable, could be performed simultaneously with the removal of excess nitrogen, an operation described below. The unstable nitrides form during the early stages of nitridation when there is an over abundance of nitrogen

It is necessary that the powders be distributed. This prevents a substantial number of particulate pieces from sticking together and allows the nitriding atmosphere to surround them, thereby creating a high nitrogen potential at the surface for the rapid nitriding required to create a fine dispersoid within each particle. Distribution can be accomplished in any number of ways which includes aligning the powders in a thin layer or imparting motion to them, e.g., tumbling, during nitridation. A presently preferred method employs an inclined rotary drum with ribs within the drum to constantly pick the powder up and drop it freely. To impart increased motion the drum could have hammers attached to its outer surface. Other means which impart motion include fluidized beds, free falling and vibratory columns.

The steel powder being nitrided could be ferritic or austenitic. Austenitic powder is preferred since it has greater strength at high temperatures. Moreover, nitrides in austenitic powder grow at a slower rate than do nitrides in ferritic powder. The powder used should be clean, i.e., it should have a low surface oxygen content. Powder with a thick oxide film, e.g., blue or black film, has its nitriding rate severely restricted and yields larger interparticle spacings than do clean powders. Nitriding of 5 mil clean powder should proceed faster than the nitriding of 5 mil foil, other parameters remaining the same due to geometrical considerations.

In order to avoid the formation of an excess number of chromium nitrides at the grain boundaries, it is desirable, but not always necessary, to degas and remove excess nitrogen, the amount over that necessary to react with the nitride former. Chromium nitride formation removes chromium from solid solution thus reducing the material's corrosion and oxidation resistance. Moreover, chromium nitrides will soften on exposure to high temperatures, e.g., 1,200°–1,500° F. Removal can be effected in a vacuum or by use of a purging gas non-reactive with the steel, e.g., hydrogen.

After internal nitridation, the steel powder is hot pressed into shaped members such as sheets, bar stock, tubing, and forging forms. The shaped members could consist solely of densified powder or could consist of powder pressed onto a substrate, such as a strip or sheet of corrosion or oxidation resistant alloy, e.g., 47 percent Ni, 22 percent Cr, 20 percent Fe, 9 percent Mo and residuals, chosen so as to produce articles tailored for specific applications. Additionally, certain tailored articles could be produced by mixing nitrided powder with dissimilar powder. For example, nitrided powder can be mixed with the powder of a precipitation hardening alloy, e.g., 54 percent Ni, 19 percent Cr, 11 percent Co, 10 percent Mo, 3 percent Ti, 1.5 percent Al and residuals. Articles comprising precipitation hardening alloys are stronger up to about 1,500° F. than composites consisting of only nitrided steel because the precipitation hardening alloy responds to age hardening. They also maintain a significant amount of strength at higher temperatures due to the nitride dispersoids.

The hot pressing is carried out in a nonoxidizing atmosphere at temperatures in excess of 1,600° F. and preferably within the range of 1,800°–2,200° F. At temperatures below 1,600° F., the material becomes too stiff to adequately densify and within the 1,800°–2,200° F. range, the advantages and disadvantages of high temperatures are best balanced. High temperatures advantageously give the powder greater plasticity but disadvantageously cause an increase in the rate of dispersoid growth. Heat for pressing can be retained from nitriding or degassing operations. Pressure is dependent upon the degree of compression necessary to densify the material so as to substantially eliminate pores. Pores are detrimental to the material insofar as they, like notches, are areas of pronounced stress concentration which increases the material's tendency to fail. Extrusion is the preferred method of applying pressure. It places the powder in compression and compressive forces do not cause nitrides to break loose from the matrix as do excessive tensile forces. The nonoxidizing atmosphere could be a vacuum, inert gas, e.g., argon, or reducing gas, e.g., hydrogen.

The following examples are illustrative of several embodiments of the invention. Powders having the composition and size shown below in Table I were internally nitrided at the temperatures shown in Table I for a period of about 10 minutes. All the powders contain titanium which is regarded as the superior nitride former, as noted above.

TABLE I

Powder	Composition								Powder size (mils)	Nitriding temperature (° F.)
	Cr	Ni	Ti	C	Mn	Si	B	Fe		
A	25.18	21.95	2.03	0.019	0.10	1.08	0.011	Balance	1.7–2.9	1,800
B	19.00	14.95	2.02	0.015	0.20	0.50	0.011	do	1.7–2.9	1,800
C	19.00	14 95	2.02	0.015	0.20	0.50	0.011	do	1.7–2.9	1,800
D	19.00	14.95	2.02	0.015	0.20	0.50	0.011	do	2.9–4.1	1,900
E	19.00	14.95	2.02	0.015	0.20	0.50	0.011	do	2.9–4.1	1,900
F	19.00	14.95	2.02	0.015	0.20	0.50	0.011	do	4.1–5.8	1,900
G	25.18	21.95	2.03	0.019	0.10	1.08	0.011	do	2.9–4.1	1,900
H	25.18	21.95	2.03	0.019	0.10	1.08	0.011	do	5.8–9.7	1,900

Nitriding was performed in a flowing ammonia atmosphere with the powders moving along the inclined rotary drum described above. Subsequently, the powders were placed in cans with open ends and degassed so as to remove excess nitrogen. Degassing was performed in a vacuum at 2,100° F. Powders C and E were degassed for 26 and 24 hours respectively and the other powders for four hours. After degassing the protective cans were evacuated and sealed. The canned powders were then extruded from 2,100° F. at a ratio of 23/1. Finally, the can was removed by pickling in acid.

Found below in Table II are the 0.2 percent yield strengths and the ultimate tensile strengths for the members produced from the processed powders as well as their interparticle dispersoid spacings.

TABLE II

Member	0.2% YS at 2,000° F. (K.s.i.)	U. T. S. at 2,000° F. (K.s.i.)	Interparticle spacing (microns)	Approx. final diam. of members (in.)
A	8.4	12.8	0.35–0.50	.429
B	19.4	25.2	0.23–0.32	.438
C	10.5	16.7	0.26–0.55	.431
D	20.2	25.5	0.36–0.48	.438
E	12.3	18.4	0.46–0.51	.488
F	20.4	26.7	0.38–0.53	.486
G	7.6	11.5	0.38–0.42	.416
H	6.4	10.0	0.77–1.54	.434

From the table it is seen that all the members exhibited good properties, an ultimate tensile strength in excess of 8 k.s.i. at 2,000° F. and interparticle spacings of less than 2 microns. It is noted that members B and C had higher strengths than member A although they were both produced from the same size powder under identical conditions. This is because A contained more nickel than B and C and, since nickel lowers the nitriding rate, higher nickel members have lower nitriding rates and produce nitride strengthened steels with greater interparticle spacings. It is additionally noted that member H had a lower strength than member G although they were of the same composition and were produced under identical conditions. This is because H powder was of a larger size than G powder, thereby requiring more time for nitridation and allowing for increased dispersoid growth. The interparticle spacing for member H is between 0.77 and 1.54 microns whereas the interparticle spacing for member G is between 0.38 and 0.42 microns.

Members B and D were further tested to evaluate their high temperature rupture strength characteristics. Found below in Table III are the testing temperatures as well as the rupture stress and rupture time.

TABLE III

Member	Temperature (°F.)	Rupture Stress (ks.i.)	Rupture Time (hours)
B	1400	40	23
B	1800	15	110
B	1900	11	91
B	1900	9.5	170
B	2000	9	34
B	2000	6	234
B	2100	5	49
B	2200	3.5	20.5
D	1700	18	953
D	1700	25	32
D	1700	20	196

From the table it is seen that the members exhibit good high temperatures rupture strength characteristics.

The examples set out above should be construed as exemplary only and in no way limiting. Although the members ranged from 0.416 to 0.488 inch in diameter, they could have been larger or smaller. The final size of the members is limited only by the capabilities of the pressing and handling equipment. In spite of the fact that the members were degassed so as to remove excess nitrogen and that degassing is often preferred it is not a necessary operation. Additionally, the particular temperatures employed for nitriding could have been replaced by any within the range discussed earlier and the flowing ammonia atmosphere could have been replaced by any of the nitriding atmosphere discussed earlier. Furthermore, the inclined rotary drum could have been replaced by other means for distributing the powder and the extruding, although the preferred form of hot pressing could be replaced by other forms such as stamping. Finally, the alloy powders employed could have been substituted for by other austenitic and ferritic steels and titanium could be substituted for by, other nitride formers such as those discussed earlier.

It will be apparent to those skilled in the art that the novel principles of the invention disclosed herein in connection with specific examples thereof will suggest various other modifications and applications of the same. It is accordingly desired that in construing the breadth of the appended claims they shall not be limited to the specific examples of the invention described herein.

We claim:

1. A composition consisting essentially of steel powder containing as a dispersoid therein particles of metal nitride having a free energy of formation of greater than about −21,000 cal./mole, said nitride particles being present at an interparticle spacing of less than about 2 microns.

2. A composition according to claim **1** wherein said dispersoid is a nitride of a metal from the group consisting of titanium, aluminum, vanadium and columbium.

3. A composition according to claim **1** wherein said dispersoid is titanium nitride and said powder is austenitic steel.

4. A composition according to claim **3** wherein said nitride particles are present at an interparticle spacing of less than about 0.5 microns.

5. A hot pressed steel article comprising densified powder, said densified powder comprising steel powder containing as a dispersoid therein particles of metal nitride having a free energy of formation of greater than about −21,000 cal./mole, said nitride particles being present at an interparticle spacing of less than about 2 microns.

6. An article according to claim **5** wherein said dispersoid is a nitride of a metal from the group consisting of titanium, aluminum, vanadium and columbium.

7. An article according to claim **5** wherein said dispersoid is titanium nitride and said steel powder is austenitic steel.

8. An article according to claim **7** wherein said nitride particles are present at an interparticle spacing of less than about 0.5 microns.

9. An article according to claim **5** wherein said densified powder comprises said steel powder and powder of a precipitation hardening alloy.

10. An article according to claim **5** wherein said densified powder is pressed onto a substrate.

11. An article according to claim **5** wherein said hot pressed steel article is a hot extruded steel article.

12. An article according to claim **5** having an ultimate tensile strength at 2,000° F. in excess of 8 k.s.i.

13. A method of strengthening iron alloy powder by internal nitridation, which comprises distributing steel powder containing a metal component capable of forming a nitride having a free energy of formation of greater than about −21,000 cal./mole, said metal component being present in an amount sufficient to provide, after nitriding, nitride particles as a dispersoid in said steel with an interparticle spacing of less than about 2 microns; and internally nitriding said distributed powder in a nitriding atmosphere, said nitriding atmosphere substantially surrounding said powder thereby creating a nitrogen potential at the surface of said powder.

14. A method according to claim **13** wherein said nitriding atmosphere is selected from the group consisting of ammonia substantially free of moisture and oxygen, nitrogen and mixtures thereof with each and with compatible gases.

15. A method according to claim **13** wherein said nitriding atmosphere contains nitrogen at above atmospheric pressure.

16. A method according to claim **13** wherein said internal nitriding is performed at a temperature between about 1,600° F. and the melting point of said steel.

17. A method according to claim **13** wherein said internal nitriding is performed at a temperature between about 1,700° **F. and about** 2,200° F.

18. A method according to claim **13** wherein following internal nitriding said powder is degassed to remove excess nitrogen.

19. A method according to claim **13** wherein said powder is distributed by tumbling.

20. A method according to claim **13** wherein said metal component is from the group consisting of titanium, aluminum, vanadium and columbium.

21. A method according to claim **13** wherein said metal component is titanium and said steel powder is austenitic steel.

22. A method according to claim **21** wherein said metal component is present in an amount sufficient to provide an interparticle spacing of less than about 0.5 microns.

23. A method of forming a hot pressed article comprising densified powder, which comprises: heating in a nonoxidizing atmosphere steel powder containing as a dispersoid therein particles of metal nitride having a free energy of formation of greater than about −21,000 cal./mole, said nitride particles being present at an interparticle spacing of less than about 2 microns; and densifying said powder into a coherent substantially non-porous body.

24. A method according to claim **23** wherein said steel powder is heated to a temperature in excess of 1,600° F.

25. A method according to claim **23** wherein said steel powder is heated to a temperature of from about 1,800° F. to about 2,200° F.

26. A method according to claim **23** wherein said steel powder is densified by extruding.

27. A method according to claim **23** wherein said dispersoid is a nitride of a metal from the group consisting of titanium, aluminum, vanadium and columbium.

28. A method according to claim **23** wherein said dispersoid is titanium nitride and said steel powder is austenitic steel.

29. A method according to claim **28** wherein said nitride particles are present at an interparticle spacing of less than about 0.5 microns.

30. A method according to claim **23** wherein said steel powder is mixed with powder of a precipitation hardening alloy prior to densifying.

31. A method according to claim **23** wherein said steel powder is pressed onto a substrate.

32. A method of forming a hot pressed article comprising densified internally nitrided iron alloy powder, which comprises: distributing austenitic steel powder containing titanium in an amount sufficient to provide, after nitriding, titanium nitride particles as a dispersoid in said steel with an interparticle spacing of less than about 2 microns; internally nitriding said distributed powder in a nitriding atmosphere, said nitriding atmosphere substantially surrounding said powder thereby creating a nitrogen potential at the surface of said powder; and densifying said powder into a coherent substantially nonporous body.

33. A method according to claim **32** wherein said titanium is present in an amount sufficient to provide an interparticle spacing of less than about 0.5 microns.

34. A method according to claim **32** wherein following internal nitridation said austenitic steel powder is degassed to remove excess nitrogen.

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