United States Patent

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[54] **NITRIDE-STRENGTHENED, STAINLESS STEEL**

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[52] **U.S. Cl.** **148/12,** 148/12.1, 148/12.3, 148/38

[51] **Int. Cl.** **C21d 7/00,** C22c 39/20, C22c 41/02

[58] **Field of Search** 148/38, 12, 12.1, 12.3; 75/128

[56] **References Cited**

UNITED STATES PATENTS

2,703,298 3/1955 Branson et al. 148/16

OTHER PUBLICATIONS

Dissertation Abstracts, Aug. 1966, Vol. 27, No. 2, 501–B–Chen, " Dispersion Strengthening of Iron Alloys by Internal Nitriding"

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[57] **ABSTRACT**

An article comprising at least one layer which consists essentially of a nitride-strengthened, austenitic stainless steel. The steel contains as a dispersoid therein particles of metal nitride having a free energy of formation of greater than −21,000 cal./mole, present at an interparticle spacing of less than about 10 microns and has a microstructure comprised of elongated primary grains which contain twins and sub-grains; wherein a substantial number of said primary grains are greater than 20 microns wide and substantially longer than 40 microns.

A method of forming a nitride-strengthened, austenitic stainless steel having a microstructure comprised of elongated primary grains which contain twins and sub-grains; wherein a substantial number of said primary grains are greater than 20 microns wide and substantially longer than 40 microns. It comprises the steps of: providing a nitride-strengthened, austenitic stainless steel which contains as a dispersoid therein particles of metal nitride having a free energy of formation of greater than −21,000 cal./mole, present at an interparticle spacing of less than about 10 microns; warm working the steel at a temperature below its recrystallization temperature; and annealing the steel at a temperature at or in excess of its germination temperature.

25 Claims, 5 Drawing Figures

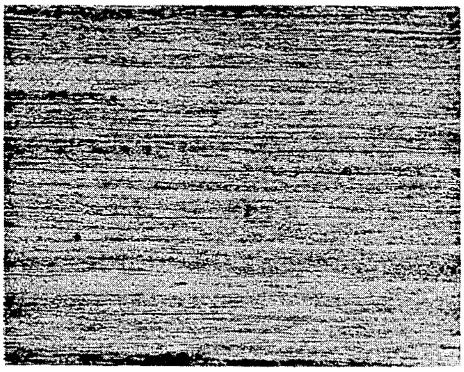


FIG. 1.

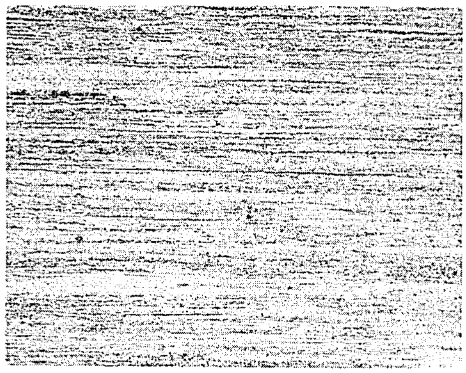
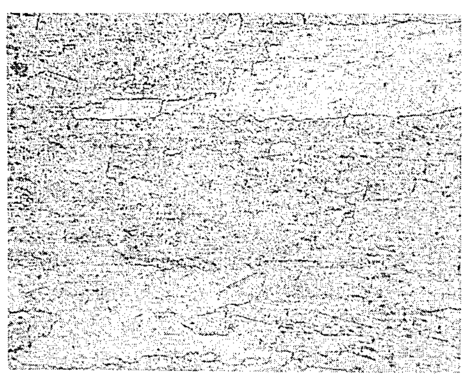


FIG. 2.



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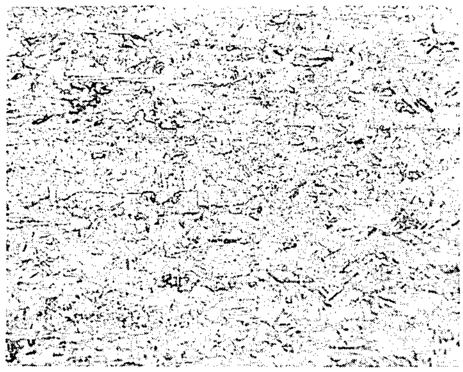

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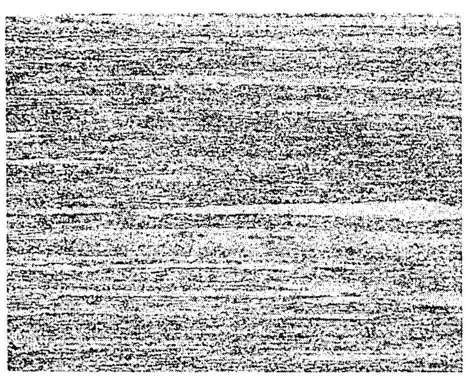

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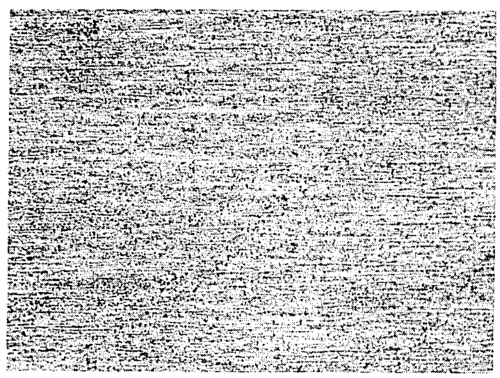
FIG. 5.



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NITRIDE-STRENGTHENED, STAINLESS STEEL

The present invention relates to a nitride-strengthened, austenitic stainless steel and more particularly to a nitride-strengthened, austenitic stainless steel with improved high temperature properties. It further related to a method for producing a nitride-strengthened, austenitic stainless steel and more particularly to a method for producing a nitride-strengthened, austenitic stainless steel with improved high temperature properties.

The aerospace industry has brought about a substantial need for material with improved high temperature properties and capabilities. A material which can fill the need is a nitride-strengthened, stainless steel which contains as a dispersoid therein particles of metal nitride, having a free energy of formation of greater; i.e., more negative, than −21,000 cal. /mole at room temperature, present at an interparticle spacing of less than about 10 microns; e.g., less than about 2 microns, and preferably less than 1 micron; e.g., less than about 0.5 micron. The metal nitride can be of a metal such as titanium, aluminum, vanadium or columbium, and is preferably titanium. U.S. Pat. application Ser. Nos. 735,186 filed on June 7, 1968 and 805,361 filed on Mar. 7, 1969, describe nitride-strengthened, stainless steel in detail along with methods for their production.

I have found that the already good properties of nitride-strengthened, austenitic chromium-containing steels, hereinafter referred to as austenitic stainless steels, can be materially improved if the steels are treated to develop a particular stable and creep-resistant microstructure. This particular microstructure is comprised of elongated primary grains which contain twins and sub-grains and is further characterized in that a substantial number of the primary grains are greater than 20 microns wide and substantially longer than 40 microns. Although not susceptible to precise numerical definition, the number of such primary grains in excess of 20 microns wide and 40 microns long should be sufficient to improve the properties of the steel; i.e., they should be sufficient to at least double the rupture life of the untreated steel at low stress levels; e.g., 5 ksi, at high temperatures; e.g., 2000°F.

It is accordingly an object of this invention to provide a nitride-strengthened, austenitic stainless steel with improved high temperature rupture strength characteristics.

It is a further object of this invention to provide a method for producing a nitride-strengthened, austenitic stainless steel with improved high temperature rupture strength characteristics.

The foregoing and other objects of the invention will be best understood from the following description, reference being had to the accompanying drawings wherein:

FIG. 1 is a photomicrograph at 250X of a nitride-strengthened, austenitic stainless steel in the as-extruded condition;

FIG. 2 is a photomicrograph at 250X of a nitride-strengthened, austenitic stainless steel which has been warm swaged and annealed subsequent to extrusion;

FIG. 3 is a photomicrograph at 250X of a nitride-strengthened, austenitic stainless steel which has been cold swaged and annealed subsequent to extrusion;

FIG. 4 is a photomicrograph at 250X of a nitride-strengthened, austenitic stainless steel and which has been annealed subsequent to extrusion; and

FIG. 5 is a photomicrograph at 250X of a nitride-strengthened, austenitic stainless steel which has been warm swaged subsequent to extrusion.

The article of the present invention is comprised of at least one layer which consists essentially of nitride-strengthened, austenitic stainless steel having high temperature properties; e.g., high temperature rupture strength characteristics, which are superior to previously known and described nitride-strengthened, stainless steel and which are attributed to the steels particular texturized microstructure which minimizes the generation of dislocations. Like all nitride-strengthened, stainless steels it contains as a dispersoid therein, particles of metal nitride, having a free energy of formation of greater than −21,000 cal. /mole at room temperature, present at an interparticle spacing of less than about 10 microns; e.g., less than about 2 microns and preferably less than 1 micron; e.g., less than about 0.5 micron. The metal nitride can be of a metal such as titanium, aluminum, vanadium or columbium, and is preferably titanium.

The particular microstructure which belongs to the nitride-strengthened, stainless steel layer of this invention is comprised of elongated primary grains which contain twins; i.e., regions in which the crystal lattice has been rotated into an orientation that is related to the orientation of the untwinned lattice in a definite symmetrical manner, and sub-grains and is further characterized in that a substantial number of the primary grains are greater than 20 microns wide and substantially longer than 40 microns. As the examples will show it is the structure which is responsible for the superior high temperature properties (properties which are better than the already good properties described in the hereinbefore referred to copending applications) of the steel. For best results the described structure should comprise at least 50 percent of the steel's microstructure but it can comprise at little as 20 percent.

As stated earlier the article of this invention can be comprised of one or more layers of nitride-strengthened, austenitic stainless steel; e.g., a number of layers of nitride-strengthened, austenitic stainless steel can be pressure bonded together as described in U.S. Pat. application Ser. No. 803,442, filed on Feb. 28, 1969. In addition, the article can comprise at least one layer of nitride-strengthened, austenitic stainless steel and one or more dissimilar layers such as a precipitation hardening alloy; e.g., 54% Ni, 19% Cr, 11% Co, 10% Mo, 3% Ti, 1.5% Al and residuals, or a corrosion resistant alloy; e.g., 47% Ni, 22% Cr, 20% Fe, 9% Mo and residuals. As a general rule each layer of nitride-strengthened, austenitic stainless steel has a rupture strength of no less than 4 ksi for 200 hours at 2,000°F when in sheet form.

The method of this invention produces a nitride-strengthened, austenitic stainless steel having the particular microstructure described above; i.e., a microstructure comprised of elongated primary grains containing twins and sub-grains which is further characterized in that a substantial number of the primary grains are greater than 20 microns wide and substantially longer than 40 microns. It comprises the steps of: providing a nitride-strengthened, austenitic stainless steel which contains as a dispersoid therein particles of metal nitride, having a free energy of formation of greater than −21,000 cal. /mole at room temperature, present at an interparticle spacing of less than about 10 microns; e.g., less than about 2 microns and preferably less than 1 micron; e.g., less than about 0.5 micron; warm working the steel at a temperature below its recrystallization temperature, and giving the steel a high temperature anneal at a temperature at or in excess of its germination temperature. The nitride contained within the steel can be of metal such as titanium, aluminum, vanadium or columbium, and is preferably titanium.

Warm working should be performed at a temperature below the recrystallization temperature of the steel being treated; i.e., the temperature at which equiaxed fine grains are formed. Material which is warm worked at a temperature of or in excess of the recrystallization temperature will not store up enough energy to insure germination during the subsequent high temperature anneal and will not form the elongated grains which are necessary if the heat treatment is to yield the desired microstructure subsequent to annealing. The exact recrystallization temperature cannot, however, be stated as it changes with variables such as the particular composition of the steel and the interparticle spacing of the metal nitride particles. A maximum warm working temperature of 2100°F is generally employed to insure maintaining a fibrous unrecrystallized grain structure during heavy warm working reductions (heavy reductions increase the likelihood of recrystallization occuring). A maximum warm working temperature of 1600°F is, however, believed to be beneficial.

Material which is warm worked at higher temperatures requires a greater reduction to cause formation of the desired structure after annealing than does material warm worked at lower temperatures; e.g., a material warm worked at 1300°F might require a 30 percent reduction whereas the same material warm worked at 1700°F might require a 45 percent reduction.

The minimum warm working temperature is dependent upon attaining a degree of plasticity which enables the steel to be worked without causing nitride particles to break loose from the matrix. It, like the recrystallization temperature, cannot be precisely set forth as it depends upon variables such as the thickness of the steel as well as the particular composition of the steel and the interparticle spacing of the metal nitride particles. As a general rule it is in excess of 800°F. A minimum warm working temperature of 1200°F is, however, preferred as it reduces the depth of edge checking.

The degree of warm working is dependent upon many variables which include the composition of the steel, its grain size and the interparticle spacing of the metal nitride particles. As a practical matter it is generally in excess of that required to reduce the cross-sectional area of the steel by 5 percent.

Any of the well known methods of warm working can be employed. The invention is not dependent upon the use of any particular method. Illustrative methods include roll pressing, flat platen pressing and swaging.

High temperature annealing is the part of the process during which the steel obtains the desired microstructure. A rapid; e.g., 5 to 60 minutes, treatment should be performed at a temperature at or in excess of the germination temperature; i.e., the temperature at which abnormal grain growth begins. Like the recrystallization temperature, the germination temperature cannot be precisely set forth as it changes with variables such as the particular composition of the steel and the interparticle spacing of the metal nitride particles. A minimum of 2300°F is often employed as the germination temperatures of nitride-strengthened, austenitic stainless steels are generally in excess of 2300°F. Germination temperatures below 2300°F are, however, characteristic of those steels with larger interparticle spacings. Steels which possess the very desirable small interparticle spacings are generally annealed at a temperature in excess of 2400°F.

The following examples are illustrative of the invention:

A number of nitride-strengthened, austenitic stainless steel samples were prepared for testing from powder containing by weight approximately 0.026% C, 0.29% Mn, 0.49% Si, 18.33% Cr, 13.50% Ni, 1.95% Ti, balance iron and incidental impurities and by volume 3.85% titanium nitride. The samples were prepared by heating the powder to 2,000°F and extruding it to a round bar in a carbon steel can at an extrusion ratio of 23:1.

The samples were then broken up into five groups; groups A, B, C, D and E. The group A sample was set aside without any further treatment. Group B samples were warm swaged 40–45 percent starting at a temperature of 1900°F and finishing at a temperature of 1300°F with intermittent reheating and subsequently annealed for one hour at 2480°F in air. Group C samples were cold swaged 40–45 percent and subsequently annealed for one hour at 2480°F in air. Group D samples were annealed for one hour at 2480°F in air. Group E samples were warm swaged 40–45 percent starting at a temperature of 1900°F and finishing at a temperature of 1300°F with intermittent reheating.

The microstructure of the groups A, B, C, D and E samples were studies and respectively recorded in FIGS. 1–5. These microstructures were taken from longitudinal sections; i.e., parallel to the major axis of the bar.

Samples from the groups were tested for their rupture strength characteristics at 2000°F. These tests are extremely important as high temperature rupture strength measurements are design criteria when choosing materials for high temperature use. Conventional tensile tests are run for a short duration and, therefore, are not as valuable as rupture strength tests for

determining the suitability of materials for prolonged use at high temperatures. The results of the tests are found below in Table I.

TABLE I

Sample	Condition	Stress (ksi)	Hours to Failure
A	as-extruded	5	62.3
B_1	warm swaged and annealed	5	900*
B_2	warm swaged and annealed	6	202
C_1	cold swaged and annealed	5	35.9
C_2	cold swaged and annealed	6	7.1
C_3	cold swaged and annealed	7	2.4
D	annealed	5	45.2
E_1	warm swaged	5	97.6
E_2	warm swaged	7	14.6

*did not fail after 900 hours

From the results one can observe the particularly good behavior of the samples which were warm swaged and annealed. Sample B_1 which was tested at 5 ksi did not fail after 900 hours whereas sample A failed after 62.3 hours, sample C_1 failed after 35.9 hours, sample D failed after 45.2 hours and sample E_1 failed after 97.6 hours at 5 ksi. Furthermore, sample B_2 which was tested at 6 ksi did not fail until 202 hours passed, whereas sample C_2 which was tested at 6 ksi failed after 7.1 hours.

The photomicrographs confirmed that the already good properties of nitride-strengthened, austenitic stainless steels can be materially improved if the steels are given a microstructure comprised of elongated primary grains which contain twins and sub-grains. FIG. 2 which is the photomicrograph of the warm swaged and annealed samples; i.e., samples B_1 and B_2, is comprised of elongated primary grains which contain twins and sub-grains and is further characterized in that a substantial number of the primary grains are greater than 20 microns wide and substantially longer than 40 microns. To the contrary; FIG. 1 which is the photomicrograph of the as-extruded sample; i.e., sample A, is comprised of fibrous grains which are approximately 2 to 20 microns wide and 300–1000 microns long; FIG. 3 which is the photomicrograph of the cold swaged and annealed samples; i.e., samples C_1, C_2 and C_3, is comprised of mostly equiaxed small grains; FIG. 4 which is the photomicrograph of the annealed sample; i.e., sample D, is comprised of very fine grains; and FIG. 5 which is the photomicrograph of the warm swaged samples; i.e., samples E_1 and E_2, is comprised of very thin; e.g., less than 10 microns, elongated grains having a length of width ratio considerably higher than the as-extruded sample; i.e., sample A.

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.

I claim:

1. An article comprising at least one layer which consists essentially of a nitride-strengthened, austenitic stainless steel containing as a dispersoid therein particles of metal nitride present at an interparticle spacing of less than about 10 microns and having a free energy of formation of greater than −21,000 cal. /mole at room temperature; said nitride-strengthened austenitic stainless steel having a microstructure comprised of elongated primary grains which contain twins and sub-grains, a substantial number of said primary grains being greater than 20 microns wide and substantially longer than 40 microns.

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

3. An article according to claim 1 wherein said dispersoid is titanium nitride.

4. An article according to claim 1 wherein said dispersoid particles are present at an interparticle spacing of less than about 2 microns.

5. An article according to claim 1 wherein said dispersoid is titanium nitride and wherein said titanium nitride particles are present at an interparticle spacing of less than about 1 micron.

6. An article according to claim 1 wherein said dispersoid is a nitride of metal from the group consisting of titanium, aluminum, vanadium and columbium and wherein said dispersoid particles are present at an interparticle spacing of less than about 0.5 micron.

7. An article according to claim 1 wherein said elongated primary grains comprise at least about about 20 percent of said microstructure.

8. An article according to claim 1 wherein said elongated primary grains comprise at least about 50 percent of said microstructure.

9. An article according to claim 7 wherein said dispersoid is titanium nitride wherein said titanium nitride particles are present at an interparticle spacing of less than about 2 microns.

10. An article according to claim 8 wherein said dispersoid is a nitride of a metal from the group consisting of titanium, aluminum, vanadium and columbium and wherein said dispersoid particles are present at an interparticles spacing of less than about 1.0 micron.

11. An article according to claim 1 including at least one layer which is dissimilar to nitride-strengthened, austenitic stainless steel.

12. An article according to claim 1 wherein each layer of nitride-strengthened, austenitic stainless steel has a rupture strength of no less than about 4 ksi for 200 hours at 2000°F.

13. A method of improving the high temperature properties of nitride-strengthened, austenitic stainless steel which comprises the steps of: providing a nitride-strengthened, austenitic stainless steel containing as a dispersoid therein particles of metal nitride present at an interparticle spacing of less than about 10 microns and having a free energy of formation of grater than −21,000 cal. /mole at room temperature; warm working said steel at a temperature below its recrystallization temperature; and annealing said steel at a temperature at least equal to its germination temperature.

14. A method according to claim 13 wherein said warm working is at a temperature of from about 800°F to about 2,100°F.

15. A method according to claim 13 wherein said annealing is at a temperature of at least about 2,300°F.

16. A method according to claim 13 wherein said dispersoid is a nitride of a metal from the group consisting of titanium, aluminum, vanadium, and columbium.

17. A method according to claim 13 wherein said dispersoid particles are present at an interparticle spacing of less than about 2 microns.

18. A method according to claim 17 wherein said dispersoid is titanium nitride.

19. A method according to claim 17 wherein said warm working is at a temperature which does not exceed a temperature of about 2,100°F.

20. A method according to claim 19 wherein said warm working is at a temperature of from about 1200°F to about 2,100°F.

21. A method according to claim 19 wherein said warm working is at a temperature of from about 800°F to about 1600°F.

22. A method according to claim 17 wherein said annealing is at a temperature of at least about 2300°F.

23. A method according to claim 22 wherein said annealing is at a temperature of at least about 2400°F.

24. A method according to claim 13 wherein said dispersoid is a nitride of a metal from the group consisting of titanium, aluminum, vanadium, and columbium and wherein said dispersoid particles are present at an interparticle spacing of less than about 0.5 micron.

25. A method according to claim 13 wherein said dispersoid is titanium nitride and wherein said titanium nitride particles are present at an interparticle spacing of less than about 1 micron.

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