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[54] **METHOD OF IMPROVING NITRIDE-STRENGTHENED STAINLESS STEEL PROPERTIES**
17 Claims, 1 Drawing Fig.

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[50] Field of Search 148/12.1, 16.6, 37

[56] **References Cited**

UNITED STATES PATENTS

2,300,274	10/1942	Dahl et al.	148/16
2,703,298	3/1955	Branson et al.	148/16

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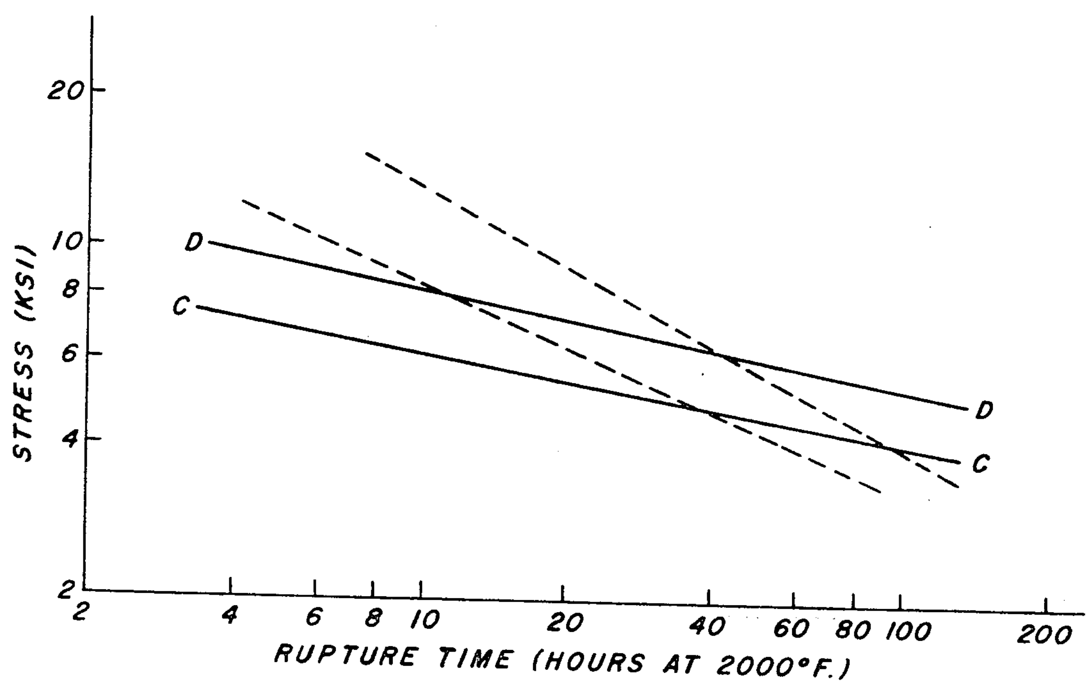
ABSTRACT: A method for improving the properties of nitride-strengthened, stainless steel containing as a dispersoid therein particles of metal nitride which are present at an interparticle spacing of less than about 10 microns and which have a free energy of formation of greater than about −21,000 cal/mol. The method comprises the steps of heating the steel to a temperature which is generally in excess of 800° F. and subsequently compressing it. Pressure is conveniently applied by roll pressing and is generally sufficient to compress the member by at least 5 percent.

A compressed nitride-strengthened, stainless steel article substantially free of pores and containing as a dispersoid therein particles of metal nitride which are present at an interparticle spacing of less than about 10 microns and which have a free energy of formation of greater than about −21,000 cal/mol.



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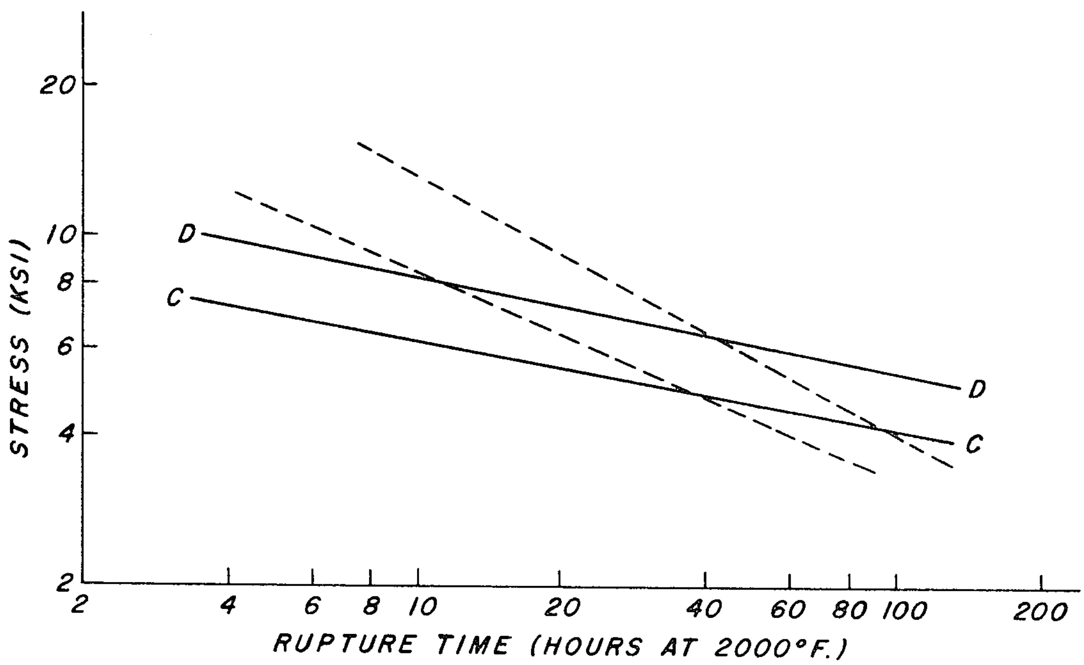

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METHOD OF IMPROVING NITRIDE-STRENGTHENED STAINLESS STEEL PROPERTIES

The present invention relates to a nitride-strengthened, stainless steel with improved properties and to a process for attaining them and more particularly to a nitride-strengthened, stainless steel with improved high-temperature rupture strength characteristics and to a process for attaining them.

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 is described in U.S. Pat. application No. 735,186 filed on June 7, 1968, hereinafter referred to as the copending application. It is a nitride-strengthened, austenitic stainless steel containing as a dispersoid therein particles of metal nitride present at an interparticle spacing or less than about 10 microns, preferably less than about 2 microns. The nitride has a free energy of formation greater than about −21,000 cal./mole and can be of a metal such as titanium, aluminum, vanadium or columbium, preferably titanium. A method for producing nitride-strengthened, stainless steel is also described in the above-referred-to copending application. It comprises, the steps of providing stainless steel containing a metal component capable of forming a nitride having a free energy of formation of greater than about 21,000 cal./mole in an amount sufficient to provide, after nitriding, nitride particles as a dispersoid in the steel with an interparticle spacing of less than about 10 microns and heating the steel at a temperature between 1,600° F. and its melting point in a nitrogen or nitrogen containing atmosphere, such as ammonia.

We have found that the already good properties of nitride-strengthened, stainless steel can be improved by a compressing operation. Compressing closes pores which may exist within the material, thus reducing its tendency to fail, and more significantly improves the material's high-temperature rupture strength characteristics.

It is accordingly an object of this invention to provide a process for improving the properties of nitride-strengthened, stainless steel.

It is another object of this invention to provide a process for improving the properties of nitride-strengthened, stainless steel by a compressing operation.

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

The figure shows a plot of rupture time versus stress for members processed according to this invention and for members not processed in accordance with this invention.

As pointed out in the above-cited copending application, it is quite often necessary to remove excess nitrogen, the amount over that necessary to react with the metal component nitride former, from the steel so that the formation of a substantial amount of chromium nitrides is prevented. 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.

The removal of excess nitrogen can be effected in a vacuum or by the use of a purging gas nonreactive with the steel, e.g. hydrogen. Unfortunately, the removal causes pores to form within the steel. These pores increase the material's tendency to fail, as does a notch insofar as they are areas of pronounced stress concentration. Therefore, it is advantageous to compress the material after removal of excess nitrogen so as to close the pores.

In addition to closing pores compressing improves the steel's high-temperature rupture strength characteristics. This is extremely important as high-temperature rupture strength measurements are design criteria when choosing materials for high temperature use. Yield strength measurements as measured by tensile tests are meaningless for high temperature, e.g. over 800° F., material applications. This is because at temperatures over about 800° F. steel under load continuously flows and strain hardening by cold working is absent.

According to the invention material should be heated prior to compressing. Heat gives the material a degree of plasticity which enables a pressing force to compress it without causing nitride dispersoids to break loose from the matrix. As a general rule it is desirable to compress material heated to a temperature in excess of 800° F. Lower temperatures often necessitate a costly series of alternate reductions and anneals since pressure at these temperatures must be controlled so that nitrides do not break from the matrix due to excessive pressure. It is also preferable not to compress at temperatures in excess of 2,400° F. although temperatures just short of the melting temperature can be employed. Higher temperatures cause the dispersoids to grow at too fast a rate thereby increasing their interparticle spacing and consequently reducing the steel's strength. A preferred temperature range is 1,800°-2 ,200° F.

The improvement in high-temperature rupture strength characteristics attained from this invention through hot or warm compressing was highly unexpected. As a general rule these characteristics are improved by annealing so as to grow coarse, uniform equiaxed grains similar to those present in noncompressed nitride-strengthened, stainless steel rather than the nonuniform type produced by hot or warm compression. This is because any instability in structure at the service temperature favors diffusion to return the metal to a more stable condition, i.e. coarse equiaxed grains, and so tends to accelerate rupture. We therefore postulate that the improvement in high-temperature rupture strength characteristics is due to a change in the character of the grain boundaries peculiar to nitride-strengthened stainless steel which is, in turn, dependent upon the degree of pressure applied. As a practical matter it is generally in excess of that required to compress the member 5 percent.

The following examples are illustrative of the invention. Nitride-strengthened, stainless steel members having the composition and properties set out below in Table I were rupture tested at 2,000° F.

TABLE I

Composition of members (percent)							Thickness of members (mils)	Average interparticle nitride spacings
Cr	Ni	Ti	C	Mn	Si	Fe		
18	12	2–4	0.003	0.50	0.75	Bal.	5–6	0.1

The slope of their log stress versus log time is shown in the figure. It varied between the broken lines. Additional nitride-strengthened, stainless steel members of the same composition were also rupture tested but were hot rolled in accordance with this invention prior to testing. The slope of their log stress versus log time is shown in the figure by lines CC and DD. Line CC represents a member which was roll pressed at 2,100° F. with a 90 reduction in area and line DD represents a member which was roll pressed at 2,200° F. with a 50 percent reduction in area.

From the figure it is evident that the roll-pressed members exhibit a flatter slope than the members which were not compressed. They clearly show in the general direction of rolling better long-time high-temperature rupture strength characteristics than the noncompressed members. For 130 hours at 2,000° F. they show a rupture strength of no less than 4 K.s.i. The poorer high-temperature rupture strength characteristics at shorter times are attributed to the high temperatures employed for roll pressing and can be avoided by roll pressing at lower temperatures. Higher temperatures although increasing plasticity, cause nitrides to grow at the expense of small interparticle spacings upon which strength is dependent. Accordingly, the member represented by line CC should have shown better rupture strength characteristics than the member represented by line DD since it was pressed at a lower temperature but contrarily it did not. This is because it was compressed to a greater degree through additional roll passes and hence was at an elevated temperature for a longer time, thus allowing further nitride growth.

The examples set out above should be construed as exemplary only and in no way limiting. The compressed members had a nominal composition of 18 percent Cr, 12 percent Ni and 2 percent Ti but could have had other nominal compositions, i.e. 25 percent Cr, 32 percent Ni and 2 percent Ti. The members were heated to temperatures of 2,100° and 2,200° F. but could have been heated to lower temperatures, i.e. 800° F. Rolling was used to supply pressure but other forms of pressure application could be employed, e.g. platens. Furthermore, several members can be simultaneously pressed as long as a separating compound is placed between them so as to prevent bonding therebetween. The number is only limited by the capabilities of the pressing and handling equipment.

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 method of improving the properties of nitride-strengthened, stainless steel, comprising the following steps:

a. providing a nitride-strengthened, stainless steel member containing as 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 about −21,000 cal./mole;

b. heating said member; and

c. compressing said member.

2. A method according to claim 1 wherein said member is heated to a temperature in excess of about 800° F.

3. A method according to claim 1 wherein said compressing is accomplished by rolling said member.

4. A method according to claim 1 wherein said member is heated to a temperature of from about 1,800° F. to about 2,200° F. and wherein said compressing is accomplished by rolling said member.

5. A method of improving the high-temperature rupture strength characteristics of nitride-strengthened, stainless steel, comprising the following steps:

a. providing a nitride-strengthened stainless steel member containing as a dispersoid therein particles of metal nitride of a metal from the group consisting of titanium, aluminum, vanadium, and columbium, said nitride particles being present at an interparticle spacing of less than about 2 microns;

b. heating said member to a temperature of from about 800° F. to about 2,400° F; and

c. roll pressing said member.

6. A method according to claim 5 wherein said dispersoid is titanium nitride.

7. A method according to claim 5 wherein said member is heated to a temperature of from about 1,800° F. to about 2,200° F.

8. A compressed nitride-strengthened, stainless steel article having a rupture strength of no less than about 4 K.s.i. for 130 hours at 2,000° F; said steel article being substantially free of pores and containing as a dispersoid therein particles of a 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 10 microns.

9. 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.

10. An article according to claim 8 wherein said dispersoid is titanium nitride.

11. An article according to claim 8 wherein said dispersoid particles are present at an interparticle spacing of less than about 20 microns.

12. A roll-pressed nitride-strengthened, stainless steel article substantially free of pores; said steel article containing as a dispersoid therein particles of a metal nitride of a metal from the group consisting of titanium, aluminum, vanadium and columbium, said nitride particles being present at an interparticle spacing of less than about 2 microns.

13. An article according to claim 12 wherein said dispersoid is titanium nitride.

14. An article according to claim 12 wherein said steel has a rupture strength of no less than about 4 K.s.i. for 130 hours at 2,000° F.

15. An article according to claim 12 wherein said dispersoid is titanium nitride and wherein said steel has a rupture strength of no less than about 4 K.s.i. for 130 hours at 2,000° F.

16. A method according to claim 2 wherein said member is compressed at least 5 percent.

17. A method according to claim 7 wherein said member is compressed at least 5 percent.