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Anello

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[45] Date of Patent: Jan. 22, 1985

[54] **THREE-STEP TREATMENT OF STAINLESS STEELS HAVING METASTABLE AUSTENITIC AND MARTENSITIC PHASES TO INCREASE RESISTANCE TO CHLORIDE CORROSION**

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[73] Assignee: **Westinghouse Electric Corp.**, Pittsburgh, Pa.

[21] Appl. No.: **487,485**

[22] Filed: **Apr. 22, 1983**

Related U.S. Application Data

[63] Continuation of Ser. No. 267,826, May 27, 1981, abandoned.

[51] **Int. Cl.**³ **C21D 7/06**
[52] **U.S. Cl.** .... **148/12 E**; 148/12.3; 148/39
[58] **Field of Search** .... 148/12 E, 12.3, 38, 148/136, 39; 29/DIG. 36; 72/53

[56] **References Cited**

U.S. PATENT DOCUMENTS

2,920,007	1/1960	Buckland	148/38
3,073,022	1/1963	Bush et al.	72/53
3,357,458	12/1967	Radd et al.	72/53
3,505,130	4/1970	Paul	148/39
3,730,785	5/1973	Conrad, Sr. et al.	148/39
3,844,846	10/1974	Friske et al.	148/12.3
4,086,104	4/1978	Kinoshita et al.	148/38

FOREIGN PATENT DOCUMENTS

41617	11/1978	Japan	148/12 E
711126	2/1980	U.S.S.R.	148/12.3

OTHER PUBLICATIONS

Shot Peening, American Wheelabrator & Equipment Corp., Mishawaka, Indiana, 1946, p. 15.
Shot Peening, The Wheelabrator Corporation, Mishawaka, Indiana, 1965, Eighth Edition, pp. 3, 34–37, 54, 130–133.

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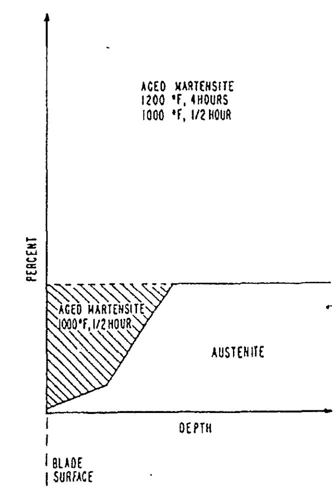
[57] **ABSTRACT**

This is a process for producing improved chloride corrosion resistance in turbine components fabricated from stainless steels which contains generally at least 1% of both a martensitic and metastable austenitic phase and comprises an initial high-intensity shot peening, followed by an aging cycle at about 980°–1020° F. for ¼–4 hours and a final (lower intensity) shot peening.

A relatively homogeneous surface of aged martensite is produced and selective attack which forms sharp pit-like defects which initiate cracks is avoided.

12 Claims, 7 Drawing Figures



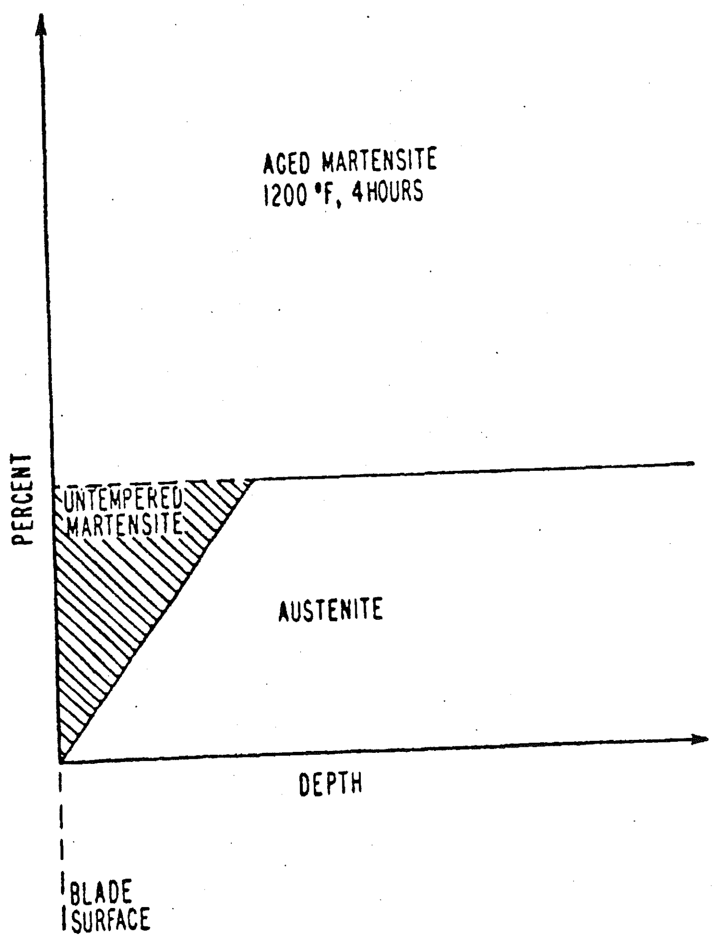

AGED MARTENSITE
1200 °F, 4 HOURS
PERCENT
UNTEMPERED
MARTENSITE
AUSTENITE
DEPTH
BLADE
SURFACE

FIG. 1

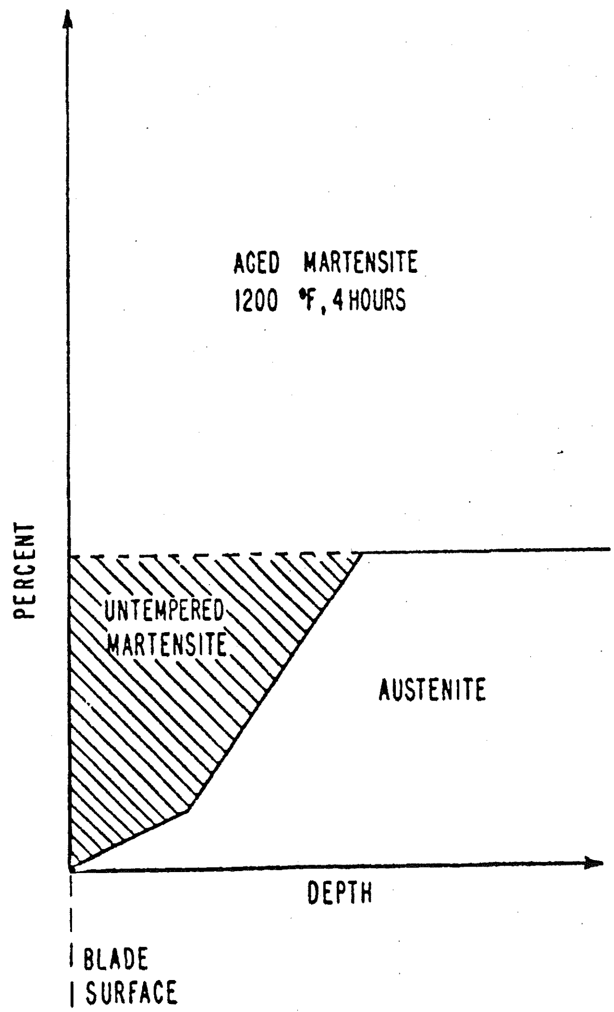

AGED MARTENSITE
1200 °F, 4 HOURS
PERCENT
UNTEMPERED
MARTENSITE
AUSTENITE
DEPTH
BLADE
SURFACE

FIG. 2

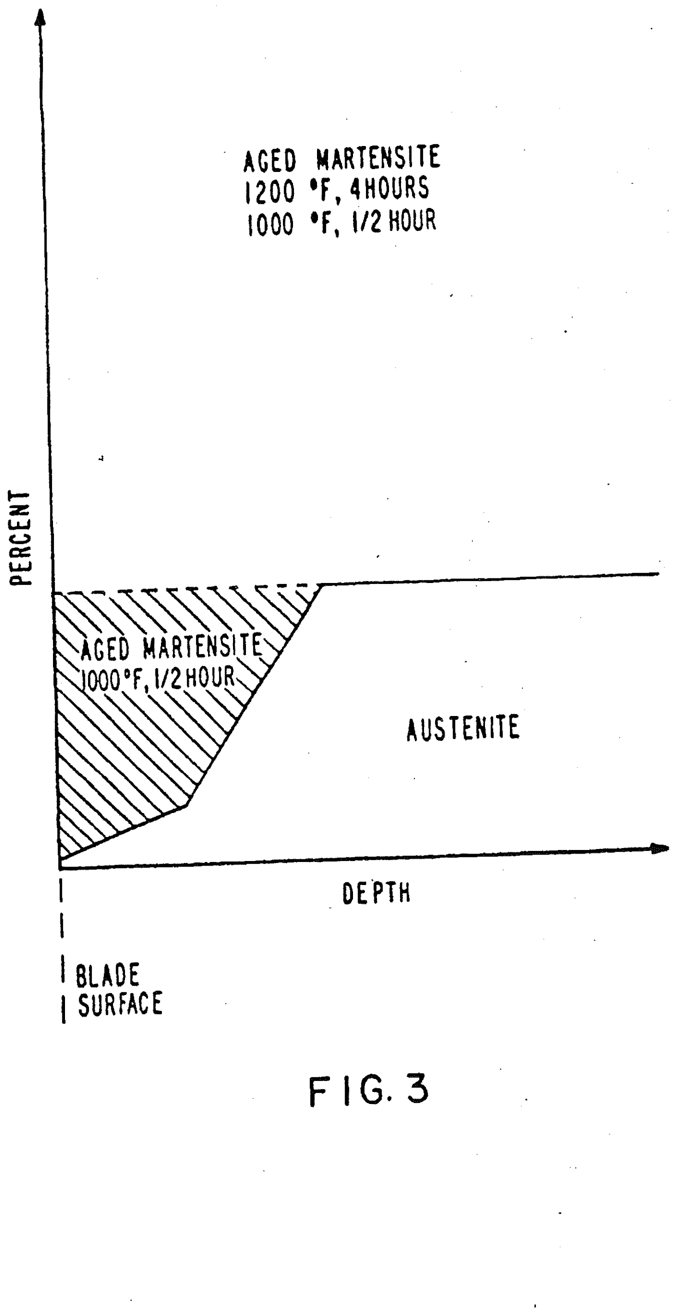

AGED MARTENSITE
1200 °F, 4HOURS
1000 °F, 1/2 HOUR
PERCENT
AGED MARTENSITE
1000°F, 1/2 HOUR
AUSTENITE
DEPTH
BLADE
SURFACE

FIG. 3

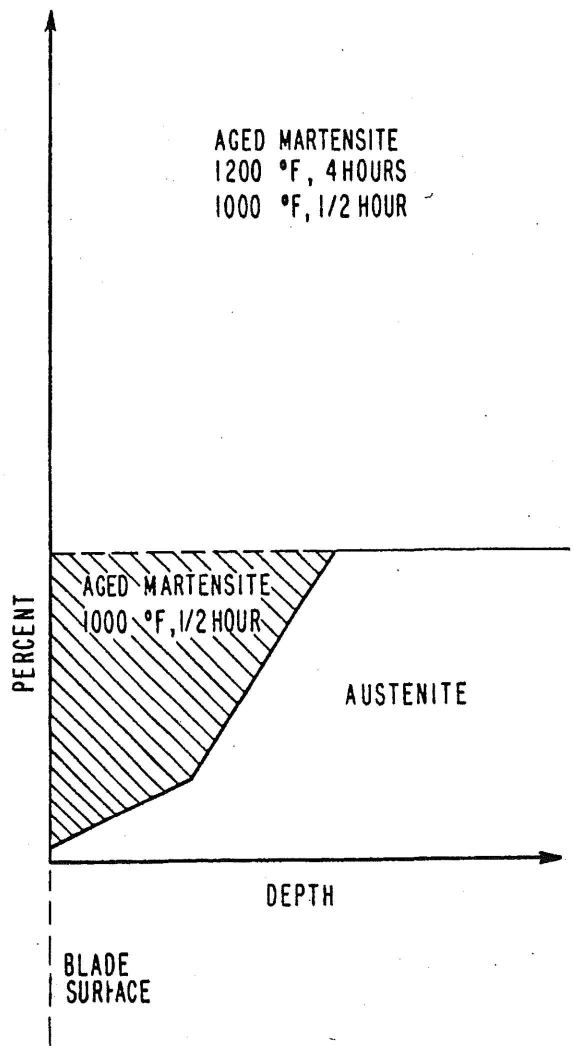

AGED MARTENSITE
1200 °F, 4 HOURS
1000 °F, 1/2 HOUR
AGED MARTENSITE
1000 °F, 1/2 HOUR
PERCENT
AUSTENITE
DEPTH
BLADE
SURFACE

FIG. 3A

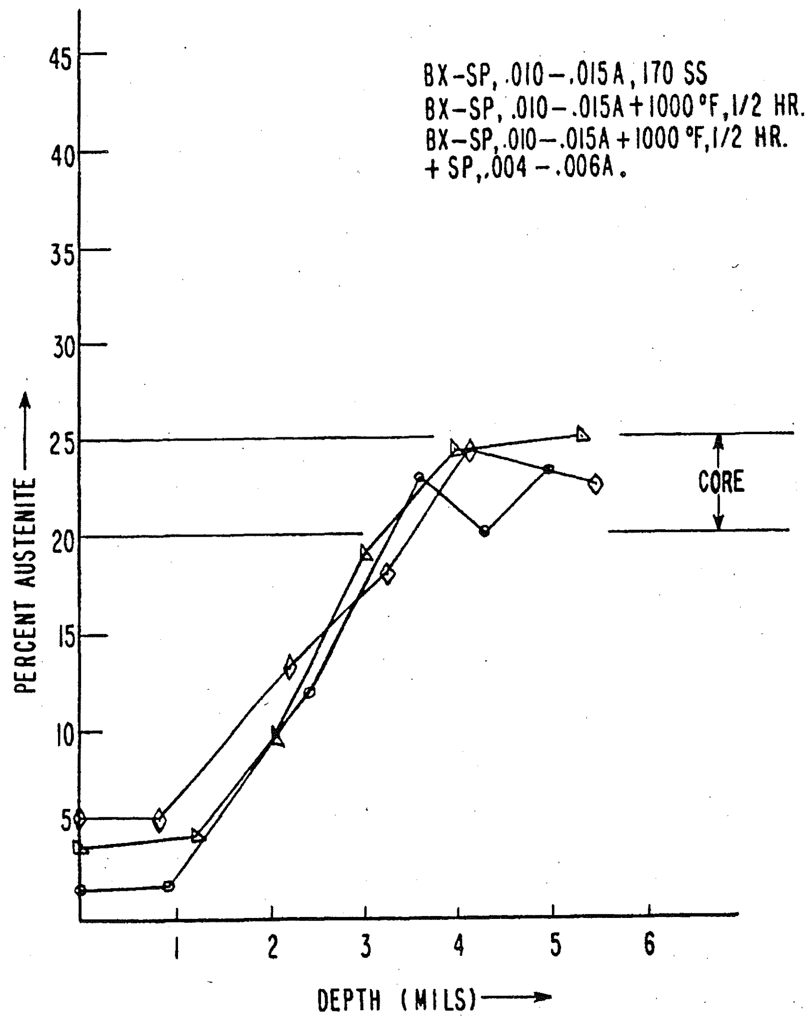

BX-SP, .010–.015A, 170 SS
BX-SP, .010–.015A + 1000°F, 1/2 HR.
BX-SP, .010–.015A + 1000°F, 1/2 HR.
+ SP, .004 – .006A.
PERCENT AUSTENITE
45
40
35
30
25
20
15
10
5
CORE
1
2
3
4
5
6
DEPTH (MILS)

FIG. 3B

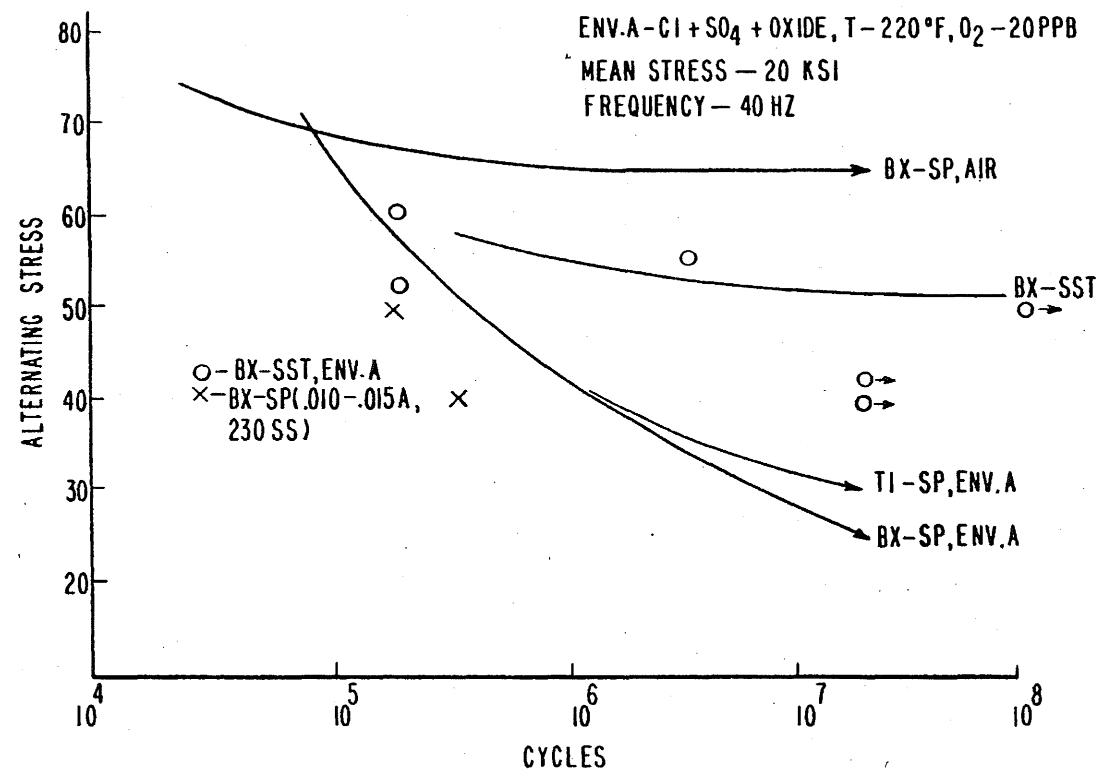

ENV.A - Cl + SO_4 + OXIDE, T - 220°F, O_2 - 20PPB
MEAN STRESS — 20 KSI
FREQUENCY — 40 HZ
ALTERNATING STRESS
80
70
60
50
40
30
20
10^4
10^5
10^6
10^7
10^8
CYCLES
BX-SP, AIR
BX-SST
TI-SP, ENV. A
BX-SP, ENV. A
○ - BX-SST, ENV. A
× - BX-SP(.010-.015A, 230 SS)

FIG. 4A

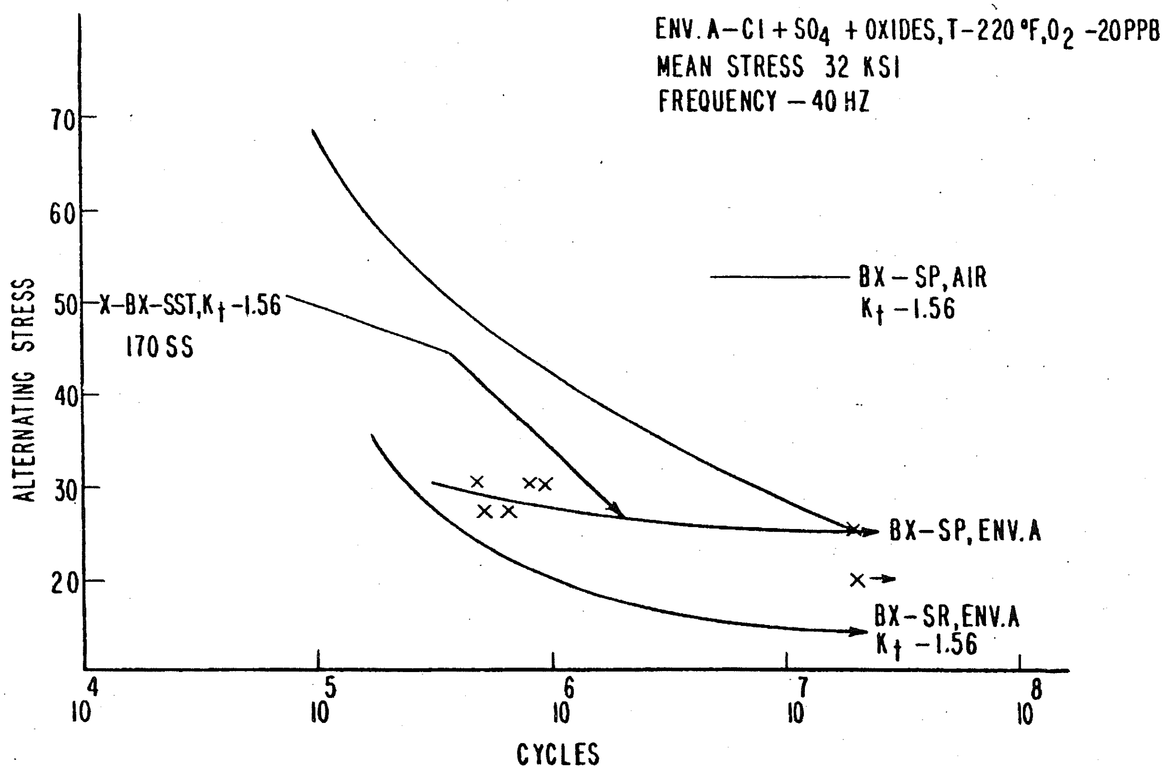

ENV. A—Cl + SO4 + OXIDES, T—220 °F, O2 —20PPB
MEAN STRESS 32 KSI
FREQUENCY — 40 HZ
ALTERNATING STRESS
70
60
50
40
30
20
X—BX—SST, Kt —1.56
170 SS
BX — SP, AIR
Kt —1.56
BX—SP, ENV. A
BX—SR, ENV. A
Kt —1.56
10^4
10^5
10^6
10^7
10^8
CYCLES

FIG. 4B

THREE-STEP TREATMENT OF STAINLESS STEELS HAVING METASTABLE AUSTENITIC AND MARTENSITIC PHASES TO INCREASE RESISTANCE TO CHLORIDE CORROSION

This is a continuation of application Ser. No. 267,826, filed May 27, 1981, now abandoned.

BACKGROUND OF THE INVENTION

This invention relates to a technique for treating stainless steel to reduce corrosion, and more particularly to stainless steels which contain both a martensitic and metastable austenitic phase, such as 17-4 PH (AISI 630 modified) or AISI type 301.

Before the development of this technique, chlorine induced corrosion assisted cracking was a very significant problem. In steam turbines, for example, chlorine ion environments had cause a large number of blade cracking incidents resulting in significant turbine downtime.

SUMMARY OF THE INVENTION

A three-step special surface treatment of stainless steel blades which contain both martensitic and austenitic phases has been developed to enhance corrosion resistance. The enhanced corrosion resistance is provided at the surface by first shot peening the surface at a high intensity to transform most of the austenite at the surface to untempered martensite; then a heat treatment is performed to convert the surface to largely all tempered martensitic; and finally the component surface is again shot peened, but at a lower intensity than in the initial step.

An embodiment of this process comprises an initial shot peening of the fabricated turbine component at an intensity of 0.010–0.015 A with 190–270 size shot. The shot peened component is then heat-treated at 980°-1020° F. for ¼–4 hours. The heat-treated component is then given a final shot peening at an intensity of 0.004–0.006 A with 70–150 size shot.

BRIEF DESCRIPTION OF THE DRAWINGS

A better understanding of the invention may be had by reference to the drawings, in which:

FIG. **1** is a graph indicating the relative percent of aged martensite, untempered martensite, and austenite as a function of depth after conventional treatment (shot peening at 0.004–0.006 A intensity);

FIG. **2** is a similar graph of percent of the phases versus depth, but after the initial shot peening step of this invention;

FIG. **3** is a similar graph of percent of the phases versus depth after the second (heating) step of this invention;

FIG. **3A** is a similar graph of percent of phases versus depth after the final shot peening step of this invention;

FIG. **3B** shows the percent austenite versus depth for a 17–4 ph stainless steel;

FIG. **4A** shows the fatigue strength of plain bar axial fatigue specimens tested in a chloride ion containing fatigue environment relative to fatigue strength in air; and

FIG. **4B** shows notched fatigue properties of various specimens under the same chloride and air environments.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

It has been found that stainless steel, which contains both martensitic and austenitic phases, have experienced pitting/cracking due to selective corrosion of the aged martensite (as opposed to equal attack on the three phases present in the microstructure's aged and unaged martensite, and austenite) when exposed to chloride ion bearing turbine environments. The selective nature of the attack results in increased sensitivity to crack initiation due to the sharp pit-like defects that are formed. Cracks propagate to such a depth that normal blade operating stresses, for example, can cause high cycle fatigue cracking and subsequent blade failure.

As can be seen from FIG. **1**, the normal shot peening at 0.004–006 A intensity changes most of the austenite at or near the surface to untempered (unaged) martensite (which, like the austenite, is not as rapidly attacked as the aged martensite which, for example, constitutes about 75 percent of the material in a 17–4 PH material). The untempered martensite in the surface layers is produced by strain transformation of austenite to untempered martensite and varying the intensity of the shot peening will vary the depth of austenite transformed.

To avoid the selective chloride attack on portions of the surface and the sharp pit-like defects which initiate cracks, the surface is converted by the process of this invention to largely all (over 95%) tempered (aged) martensite such that the corrosion occurs relatively uniformly over the entire surface (avoiding phase selective pitting and cracking).

A three-step special surface treatment is used. In the first step, the fabricated component (e.g. finished steam turbine blade) is high intensity shot peened all over (0.010–0.015 A intensity, 230 shot size, 125–300% coverage) to strain transform austenite (present in the microstructure at typically 15–35%) to unaged martensite to produce a low amount of austenite in the surface layer (to a depth of 3–5 mils). The results of this shot peening are shown schematically in FIG. **2**.

In the second step, the component is heat-treated (980°-1020° F. for ¼–4 hours) to age the material which had been transformed into unaged martensite (FIG. **3**) to cause primarily diffusion of nickel to the copper precipitate reducing the nickel in solution in the prior austenite and now aged martensite phase (austenite and untempered martensite are primarily nickel rich relative to the aged martensite). The resulting chemically homogeneous phases in the metal surface layer enhance corrosion resistance.

In the third step, the component is shot peened at lower intensity (0.004–0.006 A to regain the compressive layer) which contributes to corrosion resistance and fatigue strength benefits (FIG. **3A**).

The measured percent of austenite in a 17–4 ph steel as a function of depth after each of the three stages of the present invention is shown in FIG. **3B**.

Test specimens were exposed to a chloride ion containing fatigue testing environment (24% sodium chloride, 4.5% Na_2SO_4 solution boiling at 225° F., deaerated to 20 ppd O_2 at a pH of 7.5–8.5) to evaluate the results. As indicated in FIG. **4A**, the treatment of this invention, SST, provides a more than two times increase in fatigue strength when compared to the conventional treatment SP, (both sets of specimens tested in the aforementioned fatigue environment). As can be seen from FIG. **4B**, the notched fatigue properties of the treated material in the environment is equivalent to the standard material properties in the unnotched condition.

As can be seen from Table I below, test results for slow strain rate testing also suggests some improvement.

TABLE I

SPECIMEN PREPARATION	ENV.	SLOW STRAIN RATE TEST SUMMARY UTS (KSI)	Y.S. (KSI)	EL (%)	R.A. (%)
BX-SP (BASE-LINE)	AIR, R.T.	142	99	15.6	69.9
	"A"	115	103	6.0	19.6
SP_I - .010-.015A, 170SS 1000° F., ½ HR. SP_F - .004-.006A, 110SS	"A"	115	112	8	43.0
SAME AS ABOVE, 1000° F., 20 HRS.	"A"	123	120	10	30.1
SP_I - .010-.015A, 230SS 1000° F., ½ HR. SP_F - .004-.006A, 110SS	"A"	124	118	11	34.0
SAME AS ABOVE, 1000° F., 20 HRS.	"A"	127	123	8	37.0

ENV.A-6 gms Na_2SO_4 + 33 gms NaCl + Oxide Mixture "K", boiling (220° F.) O_2 20 ppb
SP_I - INITIAL SHOT PEENING
SP_F - FINAL SHOT PEENING

The initial high intensity shot peening is done at an intensity of 0.010–0.015 A (and preferably 0.010–0.012 A) with a shot size of 190–270 (preferably 210–250 and typically 230) and preferably with about 150% coverage. The heating is preferably done to 990°–1000° F. for about ½ to 2 hours. The final shot peening is done at an intensity of 0.004–0.006 A with 70–150 shot size (preferably 90–130 and typically 110 shot size) and preferably with 150% coverage).

What is claimed is:

1. A process for producing improved chloride corrosion resistance in turbine components fabricated from stainless steel which contains both aged martensitic and metastable austenitic phases, said process comprising:

(a) initial shot peening said fabricated component at an intensity of 0.010–0.015 A with 190–270 size shot;

(b) heating said component to about 980°–1020° F. for ¼–4 hours; and

(c) final shot peening said component at an intensity of 0.004–0.006 A with 70–150 size shot.

2. The process of claim 1, wherein said component is heated to 990°–1000° F. for ½ to 2 hours.

3. The process of claim 2, wherein 125–300% coverage is provided during both shot peenings.

4. The process of claim 3, wherein the initial shot peening is at an 0.010–0.012 A intensity with 210–250 size shot, with about 150% coverage.

5. The process of claim 4, wherein the final shot peening is with 90–130 size shot, with about 150% coverage.

6. The process according to claim 1 wherein said stainless steel further contains precipitates formed by aging.

7. The process according to claim 1 wherein said stainless steel is a 17–4 PH stainless steel.

8. The process according to claim 6 wherein said precipitates contain copper.

9. A process for producing improved chloride corrosion resistance in turbine components fabricated from stainless steel which has a surface containing both aged martensitic and metastable austenitic phases, said process comprising:

(a) initial high-intensity shot peening of said surface of said component transforming most of said metastable austenite at said surface to martensite;

(b) then heat treating to convert said surface to largely all aged martensite;

(c) and then shot peening said surface at a lower intensity than in said initial high intensity shot peening step.

10. The process according to claim 9 wherein said stainless steel surface further contains precipitates formed by aging; and after the final shot peening step said stainless steel surface is characterized by said aged martensitic phase, and precipitates containing copper.

11. The process according to claim 10 wherein said stainless steel is 17–4 PH stainless.

12. The process according to claim 10 wherein after said final shot peening step said stainless steel surface is further characterized by a low amount of austenitic phase.

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