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Friske et al.

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[54] **DESENSITIZATION OF ALLOYS TO INTERGRANULAR CORROSION**

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[52] **U.S. Cl.**..... **148/11.5 R,** 148/11.5 A, 148/12, 148/12.3

[51] **Int. Cl.**..... **C22c 39/22,** C21d 7/06

[58] **Field of Search**.... 148/11.5 R, 11.5 A, 11.5 M, 148/12, 12.3

[56] **References Cited**

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[57] **ABSTRACT**

Intergranular corrosion is prevented in sensitization susceptible alloys by severely shot peening the alloy surface so that the structure of the original grains at the surface is broken up and grain boundaries are no longer continuous, this peening treatment being done prior to exposure of the alloy to the sensitizing temperature. The method is preferred for the treatment of susceptible austenitic chromium-nickel-iron alloys, particularly the austenitic stainless steels of the 18-8 type.

7 Claims, 6 Drawing Figures

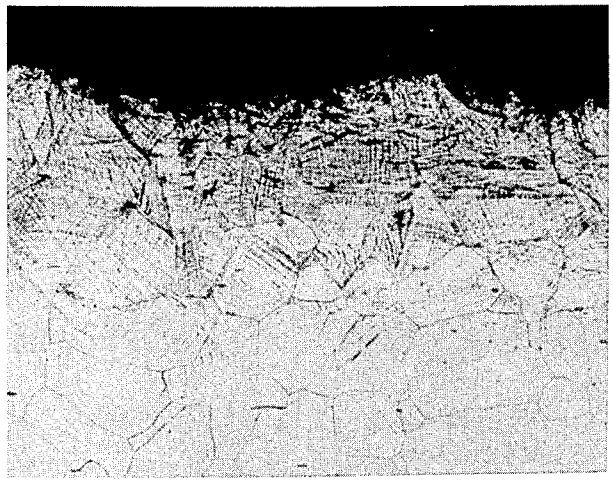


FIG. 1

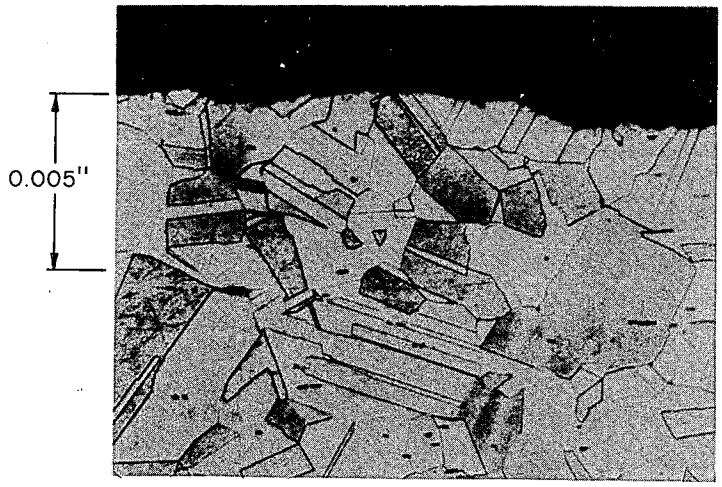


FIG. 2

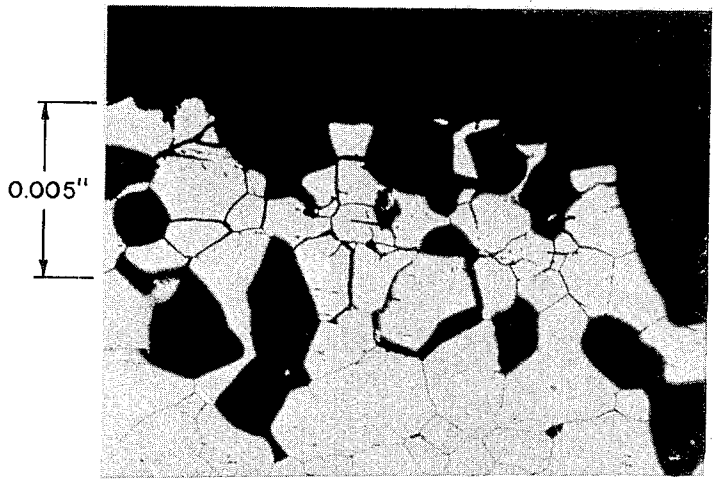


FIG. 3



FIG. 4

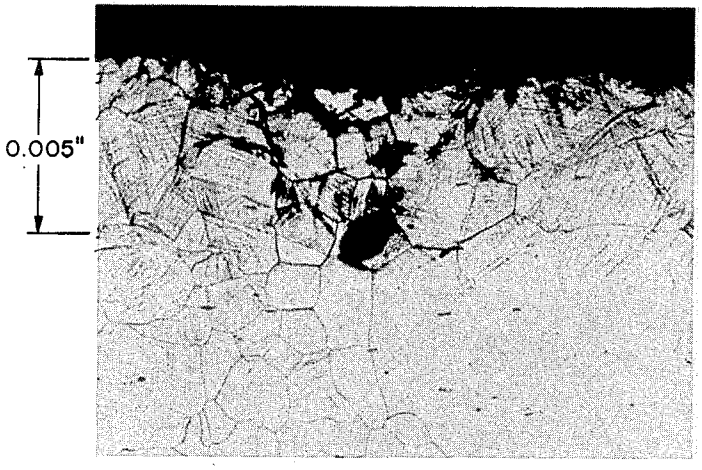


FIG. 5

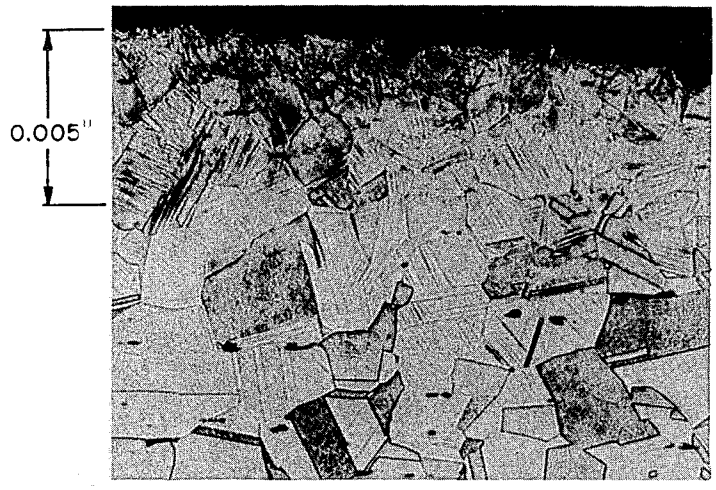
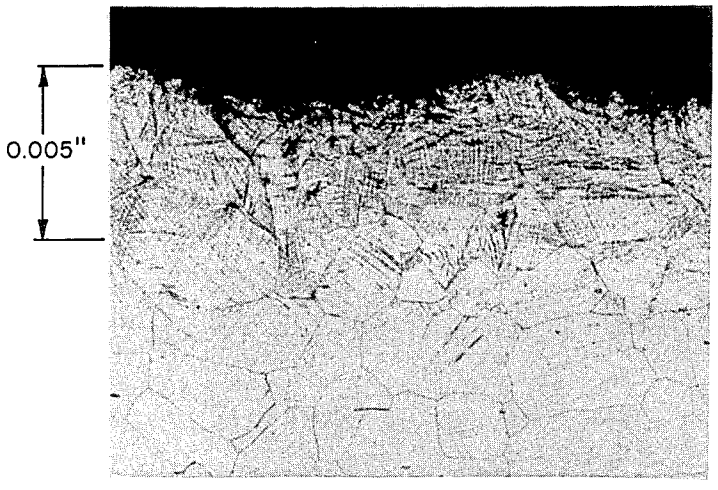


FIG. 6



DESENSITIZATION OF ALLOYS TO INTERGRANULAR CORROSION

BACKGROUND OF THE INVENTION

This invention relates to an improved method for desensitizing alloys susceptible to intergranular corrosion. It particularly relates to a method for preventing intergranular corrosion of unstabilized, sensitized austenitic stainless steels.

The annual cost of corrosion and of protection against corrosion in the United States is estimated at 8 billion dollars. Thus the prevention or control of corrosion damage economically and safely is a major problem. Metallic corrosion is a complex phenomenon, and several unique but interrelated forms of corrosion are known. The most common form of corrosion is a uniform attack over the entire exposed surface or over a large area of the metal. However, certain alloys when exposed to a temperature characterized as a sensitizing temperature become particularly susceptible to intergranular corrosion. In a corrosive atmosphere, the grain interfaces of these sensitized alloys become very reactive and intergranular corrosion results. This is characterized by a localized attack at an adjacent to grain boundaries with relatively little corrosion of the grains themselves. The alloy disintegrates (grains fall out) and/or loses its strength. The present invention is directed to the prevention of intergranular corrosion in alloys susceptible to such corrosion following exposure to a sensitizing temperature.

Intergranular corrosion is generally considered to be caused by the segregation of impurities at the grain boundaries or by enrichment or depletion of one of the alloying elements in the grain boundary areas. Thus in certain aluminum alloys, small amounts of iron have been shown to segregate in the grain boundaries and cause intergranular corrosion. Also, it has been shown that the zinc content of a brass is higher at the grain boundaries and subject to such corrosion. High-strength aluminum alloys such as the Duralumin-type alloys (Al-Cu) which depend upon precipitated phases for strengthening are susceptible to intergranular corrosion following sensitization at temperatures of about 120°C. Nickel-rich alloys such as Inconel 600 and Incoloy 800 show similar susceptibility. Die-cast zinc alloys containing aluminum exhibit intergranular corrosion by steam in a marine atmosphere. Cr-Mn and Cr-Mn-Ni steels are also susceptible to intergranular corrosion following sensitization in the temperature range of 400°–850°C. In the case of the austenitic stainless steels, when these steels are sensitized by being heated in the temperature range of about 500° to 800°C depletion of chromium in the grain boundary region occurs, resulting in susceptibility to intergranular corrosion. Such sensitization of austenitic stainless steels can readily occur because of temperature service requirements, as in steam generators, or as a result of subsequent welding of the formed structure.

Several methods have been used to control or minimize the intergranular corrosion of susceptible alloys, particularly of the austenitic stainless steels. Thus a high-temperature solution heat treatment, commonly termed solution-annealing, quench-annealing or solution-quenching, has been used. The alloy is heated to a temperature of about 1,060° to 1,120°C and then water quenched. This method is generally unsuitable for treating large assemblies, and also ineffective where welding is subsequently used for making repairs or for attaching other structures.

Another control technique for preventing intergranular corrosion involves incorporating strong carbide formers or stabilizing elements such as niobium or titanium in the stainless steels. Such elements have a much greater affinity for carbon than does chromium; carbide formation with these elements reduces the carbon available in the alloy for formation of chromium carbides. Such a stabilized titanium-bearing austenitic chromium-nickel-copper stainless steel is shown in U.S. Pat. No. 3,562,781. Or the stainless steel may initially be reduced in carbon content below 0.03 percent so that insufficient carbon is provided for carbide formation. These techniques are expensive and only partially effective since sensitization may occur with time. The low-carbon alloys also frequently exhibit lower strengths at high temperatures.

Severe cold working of the steels by cold rolling, such as to achieve an 80 percent reduction, followed by solution annealing, has been reported as preventing intergranular corrosion. Thus the cold working produces smaller grains and many slip lines which provide a much larger surface for carbide precipitation. In U.S. Pat. No. 3,437.477, an abrasion resistant austenitic stainless steel is prepared by increasing the carbon content of an AISI type 304 stainless steel to above the amount which is soluble in the austenitic matrix of the steel at 1,150°C, between 0.4 and 0.5 percent. Then following cold working to provide slip planes, the material is heated in the carbide-precipitating range. The resulting structure provides a predominantly austenitic matrix with randomly distributed massive carbides, with discontinuous smaller carbides at the grain boundaries and with fine carbides located principally on the slip planes caused by the cold working.

The effect of cold work on minimizing the intergranular corrosion of sensitized stainless steel has been reviewed by Tedmon, Jr. et al. in *Corrosion* **27**, pages 104–106 (March 1971). Because the cold-rolling treatment is not confined to the surface, but the entire bulk of the alloy must be treated, excessive work hardening often occurs. Therefore, such methods are only suitable for use with thin sheet materials and are not suitable for use with heavy plate having a thickness greater than one-fourth inch. As noted by Fontana and Green in *Corrosion Engineering*, McGraw-Hill, 1967, New York, page 64, cold working is not considered a recommended or practical procedure for controlling intergranular corrosion.

SUMMARY OF THE INVENTION

It is an object of the present invention to provide an improved, simple, and relatively inexpensive method for desensitizing or stabilizing alloys susceptible to intergranular corrosion following temperature sensitization, which is free from the disadvantages characterizing prior art methods. This method is particularly preferred for desensitizing austenitic stainless steels.

In accordance with the present invention, an alloy susceptible to intergranular corrosion is stabilized prior to being temperature sensitized by controllably shot peening the surface of the alloy to provide full coverage of the surface together with severe cold working of the surface so that the original grain structure is broken up and grain boundaries are no longer continuous. Gener-

ally, the grains in the surface layer to a depth of at least between about 1 and 5 mils (0.001–0.005 in.) are severely affected. Depending on the alloy being shot peened, the sensitization conditions, and the corrosive environment, lesser or greater depths of grain distortion may be required to achieve the desired desensitization.

The present process is generally applicable to the prevention of intergranular corrosion in a wide variety of alloys which are susceptible to this form of corrosion when exposed to a corrosive environment following temperature sensitization of the alloy. The present process is of particular utility for the desensitization of austenitic stainless steels of the 18-8 type.

It is considered an essential feature of the present invention that the shot peening of the surface of the alloy be of sufficient intensity so that the original grains in the surface layer, preferably to a depth of 1–5 mils or greater, are broken up and the grain boundaries are no longer continuous.

The shot-peening treatment required to achieve this desired degree of grain refinement and discontinuity will be a function of the particular alloy being treated as well as the shot-peening parameters of intensity and time.

The suitability of a given shot-peening treatment for achieving the desired dislocation and destruction of the grain boundaries is basically and readily determined by metallographic examination of a given type of alloy following shot peening, sensitization and corrosion exposure so that the shot-peening treatment may then be standardized with respect to this alloy. Any nondestructive testing technique such as X-ray diffraction, Mossbauer effect, electrical resistivity, magnetic properties, and the like, may be utilized that can be correlated with the metallographic examination so as to assess the degree of cold working obtained by a given shot-peening treatment. Thus an instrument responsive to changes in the amount of magnetic material present, such as the commercially available Severn gage, may be used to determine the change in the metallurgical structure of certain austenitic stainless steels induced by the shot-peening treatment. The Severn gage is responsive to amounts of ferritic or martensite, a magnetic phase formed in austenitic 18-8 grades of stainless steels by severe cold working. Also suitable for use with austenitic stainless steels is an eddy-current measuring instrument, commercially available as the Dermitron and Uresco instruments. These instruments reflect the changes in magnetic permeability and electrical conductance in the cold-worked surface layer. Thus readings taken on the two different types of instruments can be correlated with the metallographic examination of a given sample of an austenitic stainless steel so as to determine the desired, minimal or optimal shot-peening conditions for achieving the desired cold working so that about 1 to 5 mils of the surface layer no longer has any continuous grain boundaries. At the same time the known advantages of shot peening in preventing stress corrosion and fatigue failure will also be achieved by the more severe shot-peening treatment of the present invention required for preventing intergranular corrosion.

BRIEF DESCRIPTION OF THE DRAWING

FIG. 1 is a photomicrograph of an austenitic stainless steel prior to any shot-peening treatment;

FIG. 2 is a photomicrograph of the sample of FIG. 1 following temperature sensitization and exposure to a corrosive environment;

FIG. 3 is a photomicrograph of an austenitic stainless steel following shot peening for twice the time required to provide full coverage of the surface at an Almen intensity of 0.024;

FIG. 4 is a photomicrograph of the sample of FIG. 3 following sensitization and corrosion exposure;

FIG. 5 is a photomicrograph of an austenitic stainless steel following shot peening for four times the time to provide full coverage, and of such intensity as to provide a reading of 1.0–1.5 percent on the Severn gage; and

FIG. 6 is a photomicrograph of the sample of FIG. 5 following sensitization and corrosion exposure.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

In its broadest aspects, the present invention provides a process for preventing or markedly inhibiting intergranular corrosion in alloys susceptible to such corrosion following temperature sensitization and exposure to a corrosive environment. Such alloys, susceptible to differing degrees, include various copper-, magnesium-, and aluminum-based alloys in addition to the non-heat-hardenable single-phase chromium-nickel-iron austenitic alloys, particularly the 18-8 type austenitic stainless steel alloys. However, because of its commercial importance, the present invention will be particularly described with respect to the use of severe shot peening for the desensitization of the austenitic stainless steels of the 18-8type. These alloys are well known and have been characterized in a wide variety of types by the American Iron and Steel Institute. A description of the composition and typical properties of some representative AISI type 300 austenitic stainless steels is shown, for example, in the table appearing on pages 6–43 of Baumeister, *Mechanical Engineers' Handbook*, 6th Edition, McGraw-Hill, New York, 1958. AISI type 304 is representative of an unstabilized austenitic stainless steel of the 18-8 type and Inconel 600 is representative of a nickel-iron-chromium single-phase austenitic alloy, both of which alloys in the unpeened condition show severe intergranular corrosion following temperature sensitization, especially the 18-8 steel.

Shot peening is a well-known metallurgical process presently used for the cold working of metallic surfaces primarily to increase the fatigue life and prevent stress corrosion cracking of metal parts. It is also used to form parts or to correct their shape or to work-harden surfaces. The surface of the finished part is bombarded at a given intensity (measured in Almen units) with round steel or ceramic shot of a particular size, either in hand-held nozzles or in special machines, under controlled conditions including velocity and time. Every piece of the shot effectively acts as a tiny peening hammer. When a surface has been completely peened (100 percent coverage) at conventional intensities by the multitude of impacts, which is determined by visual inspection, the resultant stressed surface layer is in compression, thereby resisting surface tensile stresses which cause cracking. Generally, surface coverage from 100 to 200 percent (up to twice the time for full coverage) will suffice to provide the desired compressive stresses in the material being treated so as to minimize subse-

quent stress-corrosion cracking. Shot-peening coverage of the surface in excess of this is generally considered redundant in conventional practice.

In U.S. Pat. No. 3,648,498 is shown a device for peening and finishing the inside of a tube. This patent refers to several prior art shot-peening processes, and particularly to the description of shot peening found in the publication of the American Society for Metals, *Metals Handbook*, Vol. 2, 1964, pp. 398–405, which is incorporated herein by reference. Peening intensity is conventionally expressed in terms of Almen arc height, according to ASE Test J442. A thin flat piece of steel is secured to a solid block and exposed to a blast of shot, which tends to stretch the surface so that the strip will be curved when removed from the block. The extent of curvature is proportional to the peening intensity, which is a function of the weight, size, hardness and velocity of the peening particles, exposure time, type of substrate, angle of impingement, and various other factors.

In early cold-working studies of austenitic stainless steels, a type 304 stainless steel was shot blasted with cracked steel shot about one-sixteenth inch in diameter in a commercial blasting outfit. The shot blasting both preceded and followed short-term sensitization by welding. It was concluded that shot blasting before welding was of no benefit in preventing intergranular corrosion, if not actually deleterious, and the degree of improvement obtained by shot blasting after welding was not sufficient to be of real value. As a result of such a study, emphasis was placed on the use of extra low carbon stainless steel or stabilized grades of stainless steel as being practically effective means for preventing intergranular corrosion.

However, we have now unexpectedly discovered that if the unstabilized austenitic stainless steel is severely shot peened, beyond the ordinary requirements of 100 or 200 percent coverage, which is ordinarily sufficient to prevent stress corrosion, this severe shot-peening treatment prior to sensitization is also effective in preventing intergranular corrosion. The standard Almen test used commercially in the peening industry is not considered a satisfactory measure of peening effectiveness with respect to the degree of peening intensity required to provide resistance to intergranular corrosion. Thus the use of Almen intensity for the purposes of the present invention is considered limited to providing control and reproducibility of the peening shot stream but does not provide sufficient indication per se as to the effectiveness of the peening on the surface layer of the work piece itself. This effectiveness must be determined basically by metallographic examination of the treated specimen following temperature sensitization and corrosion. This examination may then be correlated with nondestructive measurements made using magnetic or eddy-current instruments.

It is considered critical in the practice of this invention that the shot peening treatment be such as to break up the grain structure in the surface so that the grain boundaries in this surface are no longer continuous, this generally requiring a depth of disturbance of the grain structure of at least 1–5 mils below the surface. Ordinarily this shot-peening treatment at conventional Almen intensities will involve far in excess of the equivalent of 200 percent coverage, surface coverage and Almen intensity per se becoming meaningless parameters in this regard for measuring effectiveness of treatment. As mentioned, correlation of the metallographic examination of the treated sample with nondestructive measuring techniques such as provided by magnetic material and eddy-current measuring instruments are useful in evaluation of the effectiveness of the shot-peening treatment. The use of a magnetic-material measuring instrument, such as the Severn gage, requires careful calibration on the same type of material. Such instruments, which use a series of calibrated magnets, are routinely used to determine the amount of magnetic ferrite present in an austenitic stainless steel weld metal. The Severn gage responds only to the ferrite content of the test piece and is essentially independent of its thickness. Such a technique is thus limited to use on those austenitic stainless steels in which ferrite is formed by a martensitic reaction during cold working or plastic deformation. For 18-8 type stainless steels, this transformation to ferrite will take place only if the cold working is accomplished below the phase transformation temperature, which is about 100°C. Where the Severn gage is applied to already existing weldments, then the ferrite already present in the weld metal must be considered in evaluating the shot-peening test results.

Eddy-current measuring instruments, such as the Dermitron and Uresco instruments, require a calibration reference standard of the same thickness and metallurgical history as the test piece, since these instruments respond to the magnetic permeability and electrical conductivity properties of the steel.

The following examples illustrate the process of the present invention and are directed to describing its preferred aspects relating to the treatment of an austenitic stainless steel of the 18-8 type. However, these examples are not intended to unduly limit the generally broad scope of the present invention in the shot-peening treatment of other susceptible alloys.

EXAMPLE 1

In a correlative investigation of sensitization behavior, three structural materials useful for continuous high-temperature service conditions within temperature-sensitization ranges were tested: types 304 and 321 stainless steels and Incoloy Alloy 800. These materials were in the form of hot-rolled, solution-annealed pickled plate. The stainless steel plates were one-fourth inch thick; the Incoloy Alloy 800 plate was about one-half inch thick. The materials were maintained at elevated temperatures of ca. 425°, 540°, and 650°C (800°, 1000°, and 1200°F resp.). Specimens were removed after exposure times of 5, 50, 500, 2500, 5000, 10,000, and 20,000 hours in an air atmosphere and evaluated metallographically for grain boundary precipitation of chromium carbides. When such a precipitation occurs, the material is "sensitized" and is susceptible to intergranular attack in corrosive atmospheres. The specimens were subjected to the oxalic acid etch test for intergranular corrosion in accordance with ASTM specification A262-70, "Detecting Susceptibility to Intergranular Attack in Stainless Steels."

The results of the tests showed that none of the alloys were sensitized by heating at 425°C for times up to 20,000 hours. All three alloys, however, were sensitized at temperatures of 540° and 650°C. Type 304 stainless steel was partially sensitized (surface only) after 50 hours at 540°C and fully sensitized after 500 hours; but at 650°C it was fully sensitized after 5 hours.

Although type 321 stainless steel is a stabilized grade and not as susceptible as the unstabilized type 304 stainless steel, it did become sensitized within 500 hours at 540°C and 50 hours at 650°C. Incoloy 800, a high-nickel Ni-Cr-Fe alloy, was sensitized after 500 hours at 540°C and after only 5 hours at 650°C. None of the alloys were desensitized by the long-term (20,000 hr) exposures at the elevated temperatures. Thus all three alloys were considered susceptible to intergranular corrosion attack for prolonged high-temperature exposure such as would occur for use in steam boilers and superheaters.

EXAMPLE 2

Since type 304 stainless steel is an unstabilized stainless steel and particularly vulnerable to intergranular corrosion following temperature sensitization, ¼-inch plate specimens of this steel were further investigated. Test samples were commercially peened using commercial peening equipment and procedures and were also peened using a modified laboratory blasting machine. The specimens were peened at various intensity levels using either conventional cast steel shot or a commercial ceramic bead process. The peened specimens were then heated at 650°C to promote the precipitation of chromium carbides, next subjected to a nitric-hydrofluoric acid test for intergranular attack, and examined metallographically by standard techniques. At the same time, the applicability of commercial nondestructive testing techniques, such as provided by a magnetic material measuring instrument (Severn gage) and an eddy-current measuring instrument (Dermitron) were evaluated. The results obtained are as shown in Table 1.

As will be noted from Table 1, a Severn gage reading of at least 0.5 percent "ferrite" appeared to be a threshold value for effective shot peening for the elimination of intergranular corrosion. A dermitron reading of below 3.5 (on a scale of 1.0–4.0, lower values indicating improvement) appeared to be a corresponding threshold value under the given set of test conditions.

EXAMPLE 3

In another series of runs, test specimens were sheared from type 304 stainless steel, ¼-inch hot-rolled, solution-annealed, pickled plate having a carbon content of 0.057%, Mn 1.56%, P 0.027%, S 0.024%, Si 0.048%, Ni 8.60%, Cr 18.85%, Cu 0.17%, and Mo 0.38%.

Peening was done commercially using grade 390 (0.0390-in. nominal diameter) ceramic beads at an air pressure of 80 psig. The Almen intensity for this condition for all specimens was determined to be 0.024 A. All peening was by manual operation. The specimens were prepared for peening by masking off all the areas except the area to be subjected to the peening blast. Areas about 2 inches square were peened at increasing times.

TABLE 1

Summary of Dermitron and Severn Gage Nondestructive Tests of Peened 304 Stainless Steel Plates

	Peening Parameters	Dermitron Reading	Severn Gage	Intergranular Corrosion
Steel-Shot Peened (Laboratory)	Unpeened	4.0	—	—
	40 psig - 2 min	3.8	<0.5% Ferrite	Yes
	70 psig - 2 min	3.5	<0.5	Yes
	100 psig - 2 min	3.1	<0.5	No
	100 psig - 4 min	2.5	1.5 – 2.0	No
	100 psig - 7 min	0.6	>3.5	No
	100 psig - 10 min	0	>3.5	No
Steel-Shot Peened (Laboratory)	Unpeened	4.0	—	—
	70 psig - 2 min	3.8	0.5 – 1.0%	Yes
	70 psig - 4 min	3.3	0.5 – 1.0	No
	70 psig - 6 min	2.9	0.5 – 1.0	No
	70 psig - 8 min	2.0	1.0 – 1.5	No
	70 psig - 10 min	1.0	1.5 – 2.0	No
Steel-Shot Peened (Commercial)	Unpeened	4.0	—	—
	20 psig - 100%	3.8	<0.5	Yes
	40 psig - 100	3.8	<0.5	Yes
	60 psig - 100	3.8	<0.5	Yes
	80 psig - 100	3.9	<0.5	Yes
	80 psig - 200	3.9	<0.5	Yes
	80 psig - 400	3.9	<0.5	Yes
Ceramic-Bead Peened (Commercial)	Unpeened	4.0	—	—
	20 psig - 100%	3.4	0.5 – 1.0%	No
	40 psig - 100	3.0	0.5 – 1.0	No
	60 psig - 100	2.9	0.5 – 1.0	No
	80 psig - 100	2.6	0.5 – 1.0	No
	80 psig - 200	1.4	2.5 – 3.0	No
	80 psig - 400	1.9	2.5 – 3.0	No

Peening was monitored using a Severn gage to determine the amount of magnetic ferrite formation.

The first test specimens were peened to 100 percent coverage, that is, the time of peening was just enough to assure that every unit area of the surface was impacted by the stream of shot. It was determined by visual inspection that 100 percent coverage was obtained in about 15 seconds. This peening time was doubled for 200 percent coverage, tripled for 300 percent, etc. as shown for specimens 1–4 in Table 2. Specimens 5–8 of Table 2 were peened without reference to surface coverage or time until the next higher level of "ferrite" was determined by the Severn gage.

The Severn gage did not respond to the lowest magnetic calibration, 0.5 percent ferrite, for the surfaces peened at 100 percent and 200 percent coverage. Surfaces peened at 300 percent and higher could be moni-

tored with the various calibrated magnets of the gage to indicate area ferrite contents of 0.5 percent and higher.

The peened areas were subsequently retested by the Severn gage and by a commercial eddy-current measuring instrument (Uresco) to correlate the amount of peening with the degree of cold work induced in the surface by the peening action. In addition, sections of the peened areas were metallographically examined in the as-peened condition and after sensitizing at about 680°C and testing for intergranular corrosion (2½ hours in a 10% $NHO_3$3% HF solution at 70°–80°C). The results obtained in the peening, nondestructive examination, and intergranular corrosion tests are shown in Table 2.

TABLE 2

Peening Test Summary

Examination		Nondestructive		
Specimen Number	Peening Coverage	% Ferrite (Severn Gage)	Eddy Current (Uresco)	Intergranular Corrosion
Reference	Unpeened	<0.5	40	Severe
1	100%	<0.5	40	Moderate
2	200%	<0.5	40	Slight
3	300%	~0.5	43	None
4	400%	0.5 – 1.0	46	None
5	—	1.0 – 1.5	48	None
6	—	1.5 – 2.0	51	None
7	—	2.5 – 3.5	73	None
8	—	4.0 – 5.0	85	None

As shown in Table 2, 0.5 percent ferrite content as measured by the Severn gage appears to be the probable threshold level for the shot-peening treatment required for obtaining immunity from intergranular corrosion. Peened surfaces indicating less than 0.5 percent ferrite content (independent of percentage coverage of the surface) were attached intergranularly in the NHO_3-HF test (after sensitizing), while those indicating 0.5 percent ferrite or higher were not attacked. A similar correlation using the eddy-current technique is also apparent, the threshold level being a reading of 43 based on a reference standard of 40 for an unpeened surface (higher eddy-current readings indicating improvement).

The several figures of the drawings show photomicrographs of the peened specimens before and after being subjected to intergranular corrosion, following sensitization. All photomicrographs are at 250 times magnification using an oxalic acid etch. In FIG. 1 is shown the Reference specimen of Table 2, which was unpeened. The grain structure and grain boundaries are clearly evident. In FIG. 2 is shown the specimen of FIG. 1 following sensitization and corrosion treatment. The corrosive degradation of the several areas extends deeply into the test specimen. In FIG. 3 is shown specimen No. 2 of Table 2 which had a peening coverage or 200 percent, showed a Severn gage reading of below 0.5 percent, and an eddy-current reading of between 40 and 42. The peening treatment was effective to completely cover the surface of the specimen, and such a treatment would, by providing residual compressive stresses, protect such a specimen from subsequent stress corrosion attack. As may be noted, while most of the grain boundaries in a shallow layer adjacent to the surface were broken up, in localized areas some grain boundaries did extend to the surface. FIG. 4 shows the specimen of FIG. 3 following sensitization and the intergranular corrosion treatment. It is noted that corrosive attack is still evident along grain boundaries which penetrate well into the specimen itself. In FIG. 5 is shown specimen No. 5 of Table 2 which was peened at coverage in excess of 400 percent until a reading on the Severn gage of 1.0–1.5 percent was obtained. The corresponding eddy-current reading was 46–48. As may be noted, the grain structure of the surface layer has been completely broken up, continuity of grain boundaries having been disrupted within the surface layer. In FIG. 6 is shown the specimen of FIG. 5 after temperature sensitization and subjection to the nitric-hydrofluoric acid corrosion attack. As may be noted, this specimen is free of intergranular corrosion.

Samples of Inconel 600, a high-nickel content Cr-Ni-Fe alloy having an austenitic structure, were similarly shot peened commercially using grade 390 ceramic beads at an air pressure of 80 psig. Non-peened samples, after sensitization at 680°C and corrosion exposure to nitric-hydrofluoric acid, showed intergranular corrosion. Samples which had been severely shot peened so that metallographic examination showed complete discontinuity of grain boundaries in the surface layer were found to be desensitized to intergranular corrosion under the same test conditions.

By practice of the present process, the phenomenon of continuous grain boundary carbide precipitation is eliminated, thereby eliminating the intergranular corrosion characteristic of austenitic stainless steels and other austenitic Cr-Ni-Fe alloys susceptible to such attack following temperature sensitization and exposure to a corrosive environment. Thus following severe shot-peening treatment, when the treated alloy is exposed to a thermal treatment at a sensitizing temperature, innocuous precipitation of carbides occurs throughout the cold-worked portion of the alloy. The process is further advantageous in that it can be effected during the course of fabrication of the metal parts, during installation, during service, during maintenance, or during combinations of the foregoing. For example, parts may be assembled in place for welding, and then these parts subjected to the severe shot-peening treatment of the present invention in the vicinity of the planned weld area prior to welding. Thus it has been found that intergranular corrosion is prevented when the severely shot-peened stainless steel component is heated in or through the sensitizing temperature range by welding, furnace heat treatment, or operational service. Thus the present process has shown that the intergranular corrosion of severely shot-peened and furnace-sensitized type 304 stainless steel, as determined by weight-loss measurements after testing in nitric-hydrofluoric acid, is comparable to that of the more expensive type 321, which is a stabilized stainless steel. The present process is of further utility because it may be used on a portable basis in local regions, such as the heat-affected zones adjacent to welds or in "low points" of a system which is subject to mechanisms which concentrate corrodants and are especially susceptible to corrosion.

It will be apparent that various other modifications and variations will suggest themselves to those skilled in this art and may be made without departing from the spirit of the present invention. Thus while we have described above the principles of our invention in con-

nection with specific materials and processes, it is to be clearly understood tha this description is made only by way of example and not as a limitation to the scope of the invention as set forth in the accompanying claims.

We claim:

1. The method of desensitizing an alloy susceptible to intergranular corrosion following exposure to a sensitizing temperature which comprises severely shot peening a surface of the alloy with sufficient intensity so as to break up the grain structure and eliminate continuous grain boundaries thereof prior to exposure of said alloy to said sensitizing temperature.

2. The method of claim **1** wherein said alloy is selected from austenitic Cr-Ni-Fe alloys.

3. The method of claim **2** wherein said alloy is an austenitic stainless steel of the 18-8 type.

4. The method of claim **1** wherein the grain boundary and grain structure disruption of said surface extends to at least about to 1–5 mils below the surface of said alloy.

5. The method of claim **4** wherein a surface of a stainless steel alloy of the 18-8 type is shot peened to desensitize it to intergranular corrosion, the required degree of shot peening being determined by a nondestructive test reading prior calibrated against metallographically examined samples of said alloy following shot-peening, sensitization and corrosive treatment thereof.

6. The method of claim **5** wherein said nondestructive test reading is obtained utilizing ferrite measuring or eddy-current measuring instrumentation.

7. The method of claim **4** wherein said disruption of said surface is obtained by utilizing ceramic beads for the shot peening.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

PATENT NO. : 3,844,846

DATED : Oct. 29, 1974

INVENTOR(S) : Warren H. Friske et al

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

Column 9, line 12, "$NHO_3$3%" should read --HNO_3-3%--;

line 21, in TABLE 2, "Examination" should be directly under "Nondestructive" so that the heading reads --Nondestructive Examination--;

line 39, "attached" should read --attacked--;

line 40, "NHO_3-HF" should read --HNO_3-HF--; and

line 58, "or" should read --of--.

Column 11, line 2, "tha" should read --that--.

Signed and sealed this 24th day of June 1975.

(SEAL)
Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents
and Trademarks