Title: HIGH PERFORMANCE CARBURIZING STAINLESS STEEL FOR HIGH TEMPERATURE USE

Abstract: A high performance stainless steel alloy component for high temperature service and method of production is provided in a ferrous alloy containing 0.05 to 0.50 wt. % C and 10 to 20 wt. % Cr. The shaped component, in the form of a high performance bearing, cam, gear or fastener, is carburized to achieve a carbon content of greater than 1.5 wt. % and preferably 2.0 to 2.5 wt. % in the case surface. The carburized component is then thermally treated by austenitizing, cooling, sub-zero cooling, tempering, followed by one or more cryogenic treatments followed by tempering. The microstructure of the component includes: (a) a working surface or case consisting predominantly of a martensitic matrix containing a large volume fraction of fine alloy carbides exhibiting high hardness and fatigue resistance, (b) a subjacent intermediate layer consisting substantially entirely of a stable, highly alloyed austenite, and (c) a core of a predominantly low carbon martensitic microstructure having a hardness higher than the intermediate layer and lower than the hardness of the working surface. The carburized and heat treated component combines high hardness, wear resistance and corrosion resistance, particularly in a rolling bearing surface while retaining ductility, high fracture toughness and strength in the core.
HIGH PERFORMANCE CARBURIZING STAINLESS STEEL FOR HIGH TEMPERATURE USE

BACKGROUND OF THE INVENTION

The present invention relates generally to corrosion resistant metal alloys which are useful at high temperatures. More particularly, the invention relates to a case hardenable, heat treatable, martensitic stainless steel alloy, particularly suited for use in high temperature corrosive environments, such as in aerospace applications, including rolling element bearings, gears, shafts and fasteners. Still more particularly, the present invention relates to a method for obtaining a unique microstructure through a novel carburizing step and subsequent heat treatment of the martensitic stainless steel alloy to achieve high surface hardness, improved impact fracture toughness, high temperature strength and fatigue resistance.

It is possible to produce high performance bearings, gears and other components with either high temperature strength, corrosion resistance or both, using conventional thermal treatment methods. M50 steel, for example, a type of "high speed" tool steel, has a useful hardness at operating temperatures up to about 500°F (260°C). The martensitic stainless steel type 440C has moderate corrosion resistance but is limited in operating temperature to about 300°F (150°C). A third alloy, BG-42, has both corrosion resistance and an operating temperature range up to about 700°F (370°C).

All of these steels have in common the fact that they are "through-hardening" materials. That is, their carbon content and, therefore, their hardness are uniform throughout their cross section. Such high carbon materials are lacking in fracture toughness, the ability to resist catastrophic fracture under high loads. For aerospace and other highly demanding applications, it is highly desirable that such components consist of a hard, fatigue- and wear-resistant surface and a lower strength but much tougher core. This combination of properties is most readily achieved through "case hardening" such as in carburizing, carbonitriding or nitriding.

High temperature bearing and gear alloys for the next generation of aircraft engines and transmissions require good corrosion resistance and high surface
hardness for wear resistance while maintaining a core with good fracture toughness, ductility and impact toughness. The frequently specified SAE Aerospace Material Specification AMS 6491 (M50) alloy provides good wear resistance but is deficient in both fracture toughness and corrosion resistance. AMS 6278 (M50-NiL) provides the excellent fracture toughness needed but fails to provide optimal wear resistance and is deficient in corrosion resistance for high temperature applications. Thus, there is an increasing demand for alloys combining all these characteristics for both present and future aerospace applications as thrust ratings and fuel efficiencies improve.

CSS-42L™, developed and patented by Latrobe Steel Company, is a highly alloyed 14 wt.% chromium carburizing steel alloy designed to combine hot hardness, wear resistance and corrosion resistance of the rolling element surface while retaining ductility, high fracture toughness and strength in the core. The alloy was designed particularly for use in bearing applications and carburized components but may also be adapted for use in cams, shafts, bolts, gears and other parts mainly for use at high temperatures and/or corrosive atmospheres. The CSS-42L™ alloy forms the subject matter of U.S. Patent No. 5,424,028 to James Maloney and Colleen Tomasello. The ‘028 Maloney et al. patent discloses that the CSS-42L™ alloy may be case hardened by conventional gas carburizing and hardened by a special heat treatment. Conventional carburizing achieves a carbon content of about 0.5 to 0.7 wt.% in the surface case.

Steels which possess an inherent resistance to corrosion are typically alloyed with a significant proportion of chromium, viz., 12 wt.% or more. Because of the nature of the oxide layer which forms on these steels during conventional atmosphere carburizing, carbonitriding or nitriding of these steels, it is very difficult to reliably produce a satisfactory case hardened layer on them. One technique which has been shown to be effective in overcoming this difficulty is that of intentionally "pre-oxidizing" the components in an air atmosphere at high temperatures, 1500° to 1800°F (815° to 985°C), for example. A less impermeable layer of oxide is formed by this method, so that case hardening may be more readily accomplished. Pre-oxidation has several practical drawbacks, however, including the extra processing
time required to heat and cool the parts as well as the dimensional changes which result from the surface scaling and warping which can occur.

The use of vacuum carburizing, plasma-assisted vacuum carburizing, carbonitriding or nitriding techniques are known to be an effective approach to surface hardening corrosion-resistant steels without the above-mentioned drawbacks. Because the furnace atmosphere involved in these techniques does not contain oxygen-bearing gas species, no oxide layer is formed to interfere with the case hardening process. The presence of the plasma "glow discharge" in this type of process has been shown to substantially accelerate the rate of formation of the modified case layer.

Case hardening of highly alloyed stainless steel by use of a carbon and/or nitrogen plasma process is known in the art as disclosed in U.S. Patent No. 5,851,313 to David Milam assigned to The Timken Company. The '313 Milam patent discloses that the carbon content of the hardened case surface should not exceed 0.98% by weight when processing bearing components made from stainless steel alloys containing 0.05% to 0.50% by weight carbon and containing at least 11% by weight chromium.

Thus, it is known in the art that highly alloyed chromium-containing stainless steels which can achieve both corrosion resistance and good elevated temperature properties can be successfully case-hardened to possess the desirable combination of a hard, fatigue- and wear-resistant case while maintaining a lower strength but tougher core. Nevertheless, processing techniques which are based on conventional operating parameters (carburizing to a 0.5 to 0.7 wt.% surface carbon aim) lead to less than optimal and even highly unsuccessful results. These shortcomings of the prior art are overcome by the present invention.

The present invention provides a unique carburizing/hardening method which leads to superior surface hardness, both at room temperature and at elevated temperatures, up to 1000°F (540°C), as well as rolling contact fatigue resistance surpassing that of other advanced bearing materials. In addition, highly alloyed stainless steel materials treated according to the invention develop beneficial
compressive residual stresses in the surface layer and are not plagued by the occurrence of cracks during heat treating, as are shaped articles treated by the conventional practices of the prior art.

Still further, the novel carburizing and heat treatment of the present invention provides a unique microstructure and hardness profile in highly alloyed chromium-containing steels such as CSS-42L™ alloy steel. In this manner, the present invention provides a process for treating a highly alloyed chromium-containing steel to achieve superior high temperature properties, including a case with exceptional hardness to resist fatigue and wear to a sufficient depth to support the applied loads; hardness retention at elevated temperatures; and a favorable residual stress profile below the case surface layer to aid fatigue resistance and crack resistance. The invention is particularly suitable for the manufacture of bearing components as well as other high performance components which possess a hard case over a softer and more ductile core capable of withstanding high temperature service in corrosive environments.

**SUMMARY OF THE INVENTION**

These, as well as other benefits and advantages, are achieved by the present invention. Briefly stated, the invention is directed to a process for treating a highly alloyed chromium containing steel article comprising the steps of case hardening the steel article by carburizing or carbonitriding to achieve a total actual carbon content of 1.5 wt.%, preferably 2.0 wt.% up to 2.5 wt.% or more by weight or greater at the surface; austenitizing at 1950° to 2100°F (1065° to 1150°C); quenching; stress relieving tempering, if needed; and sub-zero cooling and tempering in one or more cycles to achieve optimized final properties. The process provides a unique microstructure profile in the article comprising a working surface of the case consisting of a predominantly martensitic matrix containing a large volume fraction of fine spherical alloy carbides. This structure provides the exceptional hardness and fatigue resistance of the material. The surface layer, likewise, contains beneficial compressive stresses with a freedom from cracking during subsequent processing. The carbon content in the surface layer or case is greater than 1.5 wt.% and preferably between 2.0 wt.% to 2.5 wt.% carbon. Beneath the hard, working surface layer is an intermediate
layer consisting almost entirely of a stable, highly-alloyed austenite, with a much lower hardness than the surface. A predominantly low carbon martensitic core microstructure occupies the remainder of the cross section profile. The martensitic core has a hardness less than the surface but greater than the austenitic intermediate layer.

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BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a hardness profile graph and microstructure of a CSS-42L™ alloy specimen carburized and heat treated according to the present invention;

Figure 2 is a tempering curve showing the hardness of the carburized case of CSS-42L™ specimens at various tempering temperatures, previously austenitized at 2050°F (1121°C); and

Figure 3 is a graph comparing the hot hardness properties of case carburized CSS-42L™ alloy specimens with other comparative alloys M50NiL, M50 and AISI 440C.

DETAILED DESCRIPTION OF THE INVENTION

The present invention concerns the carburization and heat treatment of highly alloyed chromium containing ferrous alloys, including CSS-42L™ alloy of U.S. Patent No. 5,424,028 (Latrobe Steel Company), Pyrowear™ 675 alloy of U.S. Patent No. 5,002,729 (Carpenter Technology Corp.) and AISI 420. The compositional ranges of these alloys are set forth in Table 1 below.
<table>
<thead>
<tr>
<th></th>
<th>CSS-42L™ U.S. Patent No. 5,424,028</th>
<th>PYROWEAR 675™ U.S. Patent No. 5,002,729</th>
<th>AISI 420</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>0.10 to 0.25</td>
<td>0.05 to 0.1</td>
<td>0.15</td>
</tr>
<tr>
<td>Mn</td>
<td>1.0 max.</td>
<td>1.5 max.</td>
<td>1.00 max.</td>
</tr>
<tr>
<td>Si</td>
<td>1.0 max.</td>
<td>1 max.</td>
<td>1.00 max.</td>
</tr>
<tr>
<td>Cr</td>
<td>13.0 to 19.0</td>
<td>11 to 15</td>
<td>12.00 to 14.00</td>
</tr>
<tr>
<td>Mo</td>
<td>3.0 to 5.0</td>
<td>1 to 3</td>
<td>n.s.</td>
</tr>
<tr>
<td>V</td>
<td>0.25 to 1.25</td>
<td>0.1 to 1</td>
<td>n.s.</td>
</tr>
<tr>
<td>Ni</td>
<td>1.75 to 5.25</td>
<td>1.5 to 3.5</td>
<td>n.s.</td>
</tr>
<tr>
<td>Co</td>
<td>5.0 to 14.0</td>
<td>3 to 8</td>
<td>n.s.</td>
</tr>
<tr>
<td>Nb</td>
<td>0.01 to 0.10</td>
<td>n.s.</td>
<td>n.s.</td>
</tr>
<tr>
<td>B</td>
<td>0.02 max.</td>
<td>n.s.</td>
<td>n.s.</td>
</tr>
<tr>
<td>N</td>
<td>n.s.</td>
<td>0.04 max.</td>
<td>n.s.</td>
</tr>
</tbody>
</table>

The carbide forming elements chromium, molybdenum, vanadium and niobium are added to provide the necessary strength, heat resistance and wear resistance. Unfortunately, they are all ferrite stabilizers. Carbon, however, is a strong austenite former at heat treating temperatures and is responsible for attaining the hardness in the heat treated condition.

Nickel and cobalt are strong austenite stabilizers which prevent formation of the undesired ferrite. The appropriate combination of nickel and cobalt compensate for the presence of the carbide forming elements which are ferrite stabilizers. Nickel results in increased fracture toughness of the alloy, but it decreases the $M_s$ temperature that may suppress martensite formation.

Cobalt, however, has the distinct advantage of decreasing the tendency for delta-ferrite formation; it further does not depress the $M_s$ temperature. Cobalt, unlike nickel, raises the $M_s$ temperature, thereby inhibiting the presence of retained austenite which is detrimental to the attainable hardness and strength.
The ultimate goals of carburizing and heat treating advanced high
temperature carburizing steels, such as the other alloys set forth in Table 1, are to:

(a) provide a case with hardness to sufficient depth to support the
applied loads; (b) achieve a high surface hardness to resist fatigue and wear;
(c) promote good hardness retention at elevated service temperatures; (d) generate a
favorable residual stress profile to aid fatigue resistance and crack growth resistance;
and (e) produce a well-dispersed carbide structure to promote surface toughness and
corrosion resistance.

Achieving these above goals is a result of producing the proper carbon
concentration profile, then controlling the concentration of carbon in solution and the
cooling rates (both post-carburizing and after hardening).

Carburizing:

To achieve the novel case hardness, microstructure and residual stress
properties of highly alloyed chromium-containing ferrous alloys, it is deemed critical
to carburize to a relatively high carbon content, namely, at levels of greater than
1.5 wt.% or more. Due to the nature of this highly alloyed material, cracking of the
carburized case was found to be a serious problem. It was discovered, however, that
when the carbon content was raised to 1.5 wt.% or more during carburization, in
accordance with the invention, the cracking of the case on cooling from carburizing was
eliminated. Preferably, the carbon content of the carburized case is greater than 1.5
wt.% and more preferably about 2.0 to 2.5 wt.%.

The post-carburization hardening to produce the novel microstructure
is most effectively carried out with the use of a vacuum furnace; however, conventional
furnaces also provide satisfactory results. If the carburizing is done in a vacuum
furnace, the temperature can be raised from the 1600° to 1800°F (870° to 985°C)
carburizing temperature directly to the austenitizing temperature of 2000° to 2050°F
(1090° to 1120°C), followed by oil quenching.

Parts requiring a double-quench (such as when gas carburizing is used)
can be hardened by preheating to 1450°F (788°C), then austenitizing at 2000° to
2050°F (1090° to 1120°C), followed by gas fan quenching in nitrogen to about 150°F (66°C) and air cooling to room temperature.

The unique microstructure and hardness profile resulting from the case carbon content and from these treatments is depicted in Figure 1. The working surface layer 2 consists of a predominantly martensitic matrix containing a large volume fraction of fine, spherical, alloy carbides. This structure provides the exceptional hardness and fatigue resistance of the material.

Below the working surface 2, the microstructure transitions to an intermediate layer 4 consisting almost entirely of a stable, highly-alloyed austenite, with a much lower hardness than the surface. A normal, predominantly low carbon martensitic microstructure of the core 6 occupies the remainder of the cross section.

The unique properties of materials which have been processed according to the present invention derive from the combination of microstructural components, or phases, which are produced in the near-surface intermediate layer. It is essential to the treatment that a higher than conventional level of surface carbon is added (greater than 1.5 wt.% C) to the treated component during the carburizing process. The extreme hardness of the surface, which contributes to the excellent fatigue- and wear-resistance of treated parts, results from a layer on the surface in which the carbon content exceeds that of the austenitic phase at the carburizing temperature. The result is a microstructure containing a multiplicity of fine, hard carbides of chromium, molybdenum, vanadium and other carbide-forming alloying elements, alone or in combination. The austenite surrounding these carbides, as a result of the removal of carbon in solution to the carbides, develops a transformation temperature (Ms, or martensite-start temperature) high enough to allow it to transform to the martensite phase when it is cooled by quenching in oil or similar suitable medium, after the carburizing treatment. This composite layer of extremely hard alloy carbides and hard, but relatively tougher, high carbon martensite constitutes an important portion of the highly durable near-surface layer. The properties of the layer are further enhanced during the following deep-freezing and tempering steps. To enhance the hardness and
dimensional stability of the treated components, it is desirable to transform as much of
the remaining austenite in the near-surface layer as possible. This is accomplished by
continuing the cooling of the quenched component by subjecting it to cryogenic
temperatures, preferably in the range from -100° to -321°F (-73° to -196°C). The
newly-formed martensite, as well as that previously formed by quenching, is further
strengthened by the precipitation of secondary-hardening alloy carbides when the
component is subsequently tempered in the temperature range from 600° to 1100°F
(315° to 595°C). For increased effectiveness, the deep freezing and tempering steps
are preferably repeated at least one more time.

At subsurface depths, intermediate to the extremely hard surface layer
and the uncarburized, low carbon core, austenite whose solubility for carbon was not
exceeded in carburizing remains. Because of the high concentration of carbon and
alloying elements in solid solution in this austenite, the martensite transformation
temperature, Ms, is too low to permit its transforming to martensite, even during the
cryogenic treatments. As a result, an intermediate layer consisting almost entirely of
retained austenite, with minor amounts of martensite and carbides, occurs. The
hardness of this intermediate layer is very much lower than that of the surface layer,
on the order of 25 to 30 HRC, as compared to 67 to 70 HRC for the case working
surface. Successful processing of materials according to this invention always includes
this intermediate layer of retained austenite in some degree. Without it, cracking
during quenching is likely, and beneficial surface compressive residual stresses are not
produced in the treated article.

The core of components processed by the disclosed treatments consists
of martensite, strengthened by solid solution alloying and secondary carbide
precipitation hardening. Typically, the core hardness of a completely treated part is in
the range of 48 to 53 HRC when manufactured from the CSS-42L™ alloy.

The addition of carbon to the near surface region can be accomplished
by gas, vacuum, and plasma-assisted methods. The preferred process embodiment
utilizes plasma-assisted carburization because it provides a simpler way to obtain the
desired 2.0 to 2.5 wt.% carbon concentration in the case while it prevents cracking since heat treatment is conducted in the same furnace.

The details of construction and operation of a plasma-assisted carburizing furnace to effect carburizing of stainless-type steels is described in great detail in U.S. Patent No. 5,851,313 to Milam assigned to The Timken Company, the disclosure of which is included by reference herein.

The unique and essential feature of carburizing to achieve the exceptional properties noted above, whether in atmosphere, vacuum, or plasma-assisted vacuum equipment, is the high carbon potential which is maintained during carburizing. In a conventional furnace, a high carbon potential which produces an end surface carbon content of at least 1.5 wt.% and preferably 2.0 to 2.5 wt.% carbon has been found to produce the desired results. In a vacuum or plasma-assisted vacuum furnace, a boost/diffuse control technique is typically used as described in the '313 Milam patent, which is incorporated herein by reference. In this case, the ratio of boost and diffuse is maintained such that the end surface carbon content of greater than 1.5 wt.% is also employed. Because of the high content of carbide-forming elements in steels suitable for processing according to the instant invention, the actual total surface carbon is surprisingly much higher than in conventional carburizing of carbon steel for the same carbon potentials. By way of example, a carbon potential which would produce a 1.3 wt.% carbon content on the surface of a carbon steel would produce a carbon content of about 2.0 wt.% or more in highly alloyed chromium-containing ferrous alloys such as CSS-42L™ when both steels are carburized in a gas carburizing furnace under the same conditions. Carburizing may be carried out at about 1600° to 1800°F (870° to 985°C) and is time dependent on the depth of case required.

The thermal history of the product immediately after carburizing is critical to preventing cracking of the parts. The parts should not be allowed to cool directly to room temperature from the carburizing temperature if cracking is to be prevented. As mentioned above, the high carbon content of 1.5 wt.% or greater in the
case minimizes the cracking problems of the prior art, particularly when the austenitizing or hardening step is conducted in the plasma furnace.

When carburizing in a conventional, integral quench furnace, the parts should be removed from the heating chamber to the atmosphere-protected vestibule where they should be allowed to cool to "black" but not below a temperature of 400°F (204°C). The parts are then removed and transferred, hot, to a furnace preheated to 1000°F (538°C). They should be soaked at a temperature of 1000° to 1200°F (538° to 650°C) for at least four hours, prior to cooling to room temperature. When carburizing in a vacuum or plasma-assisted furnace, the temperature is reduced to 1000° to 1100°F (538° to 595°C) and allowed to soak from 2-4 hours prior to quenching in a suitable media.

Carburized parts so treated may then be hardened as follows. In a protective atmosphere set at a 0.8 to 1.1% carbon potential vs. carbon steel, or in a vacuum furnace, the parts are preheated to 1450° to 1550°F (785° to 845°C) and held at temperature until equalized. The temperature is raised to 1950° to 2100°F (1065° to 1150°C) and the parts are soaked 15 to 30 minutes, then suitably quenched, for example, oil quenched in 150° to 250°F (66° to 125°C) oil, in a press quench, if dimensional control is needed, or gas fan cooled. The actual hardening temperature will determine the extent of the subsurface austenite layer and, therefore, the effective case depth. Further, the surface residual stresses will become more compressive as the hardening temperature is increased. These effects are detailed in Table 2, below.

| TABLE 2 – Effect of Austenitizing Temperature on Case Hardness and Residual Stress |
|-------------------------------------------------|------------------|------------------|
| **Austenitizing Temperature** \(^{\circ\text{F}}\) | **Residual Stress** | **Effective Case Depth** |
| \((^{\circ\text{C}})\) | **Average from indicated depth** | **to 58 HRC** |
| | \(0.25\text{-}0.50\text{mm} (0.01\text{-}0.02 \text{ in.})\) | **mm** | **(in.)** |
| 1900 | 1038 | 514.4 MPa (74.6 ksi) | 0.864 | (0.034) |
| 2000 | 1093 | -44 MPa (-6.4 ksi) | 0.711 | (0.028) |
| 2050 | 1121 | -249 MPa (-36.1 ksi) | 0.305 | (0.012) |
When the carburizing process is carried out in a vacuum or plasma-assisted vacuum furnace, hardening may be performed directly, as follows. At the end of the carburizing cycle, the furnace temperature is raised to 1950° to 2100°F (1065° to 1150°C), and held until the work has stabilized for 15 to 45 minutes, then it is suitably quenched, for example, oil quenched or N₂ gas fan quenched directly to 150° to 200°F (65° to 95°C) and cooled to room temperature. With either the conventional or vacuum furnace hardening, a stress-relieving temper at 400° to 500°F (204° to 260°C) may be applied prior to further processing.

At this point, the carburized and hardened parts are subjected to a series of cryogenic deep freezing and tempering processes to establish their final properties. When the parts have cooled to room temperature from the stress-relieving temper, deep freeze at -120° to -321°F (-73° to -196°C). Greater hardness and stability result from lower temperatures. The parts are rewarmed to room temperature, then tempered for at least two hours at a temperature of 600° to 1100°F (315° to 595°C). The cyclic steps of deep freezing and tempering should be repeated at least one more time and ideally three times.

While the above processing temperatures were developed for the CSS-42L™ type steel, it will be recognized that other chromium-containing and high alloy steels, such as those set forth in Table 1, are also suitable for processing according to these procedures and related variations thereof selected to optimize the resulting properties.

It appears that the effective case depth is inversely related to the austenitizing temperature. The austenite layer thickens and the level of compressive residual stress in the case is greatly improved by austenitizing at higher temperatures. To illustrate the effects of austenitizing temperature on residual stresses, the case depth and residual stresses were measured on samples carburized with a shallow case (i.e., short carburizing time) treatment utilizing three different austenitizing temperatures (Table 2). It can be seen that to maintain the same effective case depth with higher austenitizing temperatures, the carburizing time must be increased. The effect of the
tempering temperature on case hardness was evaluated and the results are set forth in Figure 2. For comparative purposes, the hot hardness of case carburized CSS-42L™ alloy is shown in Fig. 3 along with hot hardness values of M50 NiL, M50 and 440C treated in accordance with the invention.

Rolling Contact Fatigue Testing

The benefit of the high surface carbon surface and the intermediate austinite layer is most evident in rolling contact fatigue performance.

Specimens were prepared for rolling contact fatigue rig testing in a ball-rod tester. Blanks, machined to a 0.38 mm (0.015") oversize in diameter, were carburized to provide an effective case depth of 0.64 to 0.76 mm (0.025" to 0.030") after grinding. Rod specimens ground using an alumina wheel to a surface finish of 3.5 microinch Ra were tested at ambient temperatures with 52100 steel balls. The 52100 balls had their surface roughened by shot blasting to a 3.5 to 4.0 microinch Ra finish. The test load produced a maximum contact stress of 5,419 MPa (786 ksi). Lubrication was supplied by drip-feeding SAE-20 oil at a rate of 10 to 12 drops per minute.

No failures occurred during many CSS-42L™ test runs. Tests were suspended due to failures of the balls, test cups or machine (Table 3).

<table>
<thead>
<tr>
<th>TABLE 3 - Ball-on-Rod Fatigue Results of CSS-42L™</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carburized Specimen #1</td>
</tr>
<tr>
<td>Cycles*</td>
</tr>
<tr>
<td>Hours</td>
</tr>
<tr>
<td>294.4</td>
</tr>
<tr>
<td>212.4</td>
</tr>
<tr>
<td>438.0</td>
</tr>
<tr>
<td>853.7</td>
</tr>
</tbody>
</table>

* Accumulated cycles is obtained by multiplying the accumulated test hours by 516024 cycles/hour.

** Reason test was discontinued.
The present invention thus provides case hardened and heat treated, highly alloyed stainless steel components such as bearing elements, gears, fasteners and the like having a unique near surface intermediate layer with an extremely hard outer working surface. These high performance components combine excellent corrosion resistance and fracture toughness with superior hot hardness, making them especially suitable for present and future aerospace applications.

While specific embodiments of the invention have been described in detail, it will be appreciated by those skilled in the art that various modifications and alternatives to those details could be developed in light of the overall teachings of the disclosure. The presently preferred embodiments described herein are meant to be illustrative only and not limiting as to the scope of the invention which is to be given the full breadth of the appended claims and any and all equivalents thereof.
WE CLAIM:

1. A process for manufacturing a case hardened stainless steel component comprising:
   (a) providing a shaped component made from a stainless steel alloy composition comprising Fe, about 0.05 to 0.50 wt.% C and about 10 to 20 wt.% Cr;
   (b) case hardening the component by one of carburizing or carbonitriding to achieve a carbon plus nitrogen content of at least 1.5 wt.% on a working surface of the article;
   (c) thermally treating the case hardened component by austenitizing, cooling, sub-zero cooling, tempering, followed by one or more deep cryogenic treatments followed by tempering; and
   (d) providing thereby a component having a working surface consisting of a predominantly martensitic matrix containing a dispersion of fine, spherical, alloy carbides having a high hardness and fatigue resistance, an intermediate layer subjacent the working surface consisting substantially entirely of a stable, highly alloyed austenitic microstructure having a lower hardness than working surface, and a core subjacent the intermediate layer, said core comprising a predominantly low carbon martensitic microstructure having a hardness higher than said intermediate layer and lower than said working surface.

2. The process of claim 1 wherein the case hardening step (b) is carried out in a plasma assisted vacuum furnace and wherein the carbon plus nitrogen content is about 2 wt.% to about 2.5 wt.% on the working surface of the article.

3. The process of claim 1 wherein the stainless steel alloy is one selected from the group consisting of CSS-42L™, PYROWEAR 675™ and AISI 420 grade steels.
4. The process of claim 1 wherein the component is one selected from the group consisting of bearings, cams, gears and fasteners.

5. The process of claim 1 wherein the case hardening step (b) is carried out in a gas atmosphere furnace and wherein the carbon plus nitrogen content is about 2 wt.% to about 2.5 wt.% on the working surface of the article.

6. The process of claim 1 wherein the thermally treating step (c) includes austenitizing at 1950° to 2100°F (1065° to 1150°C).

7. The process of claim 1 wherein the sub-zero cooling treatment of step (c) is conducted at a temperature of less than -100°F (-73°C).

8. The process of claim 1 wherein the tempering treatment following sub-zero cooling of step (c) is conducted at a temperature of 400° to 1100°F (204° to 595°C).

9. The process of claim 1 wherein the deep cryogenic and tempering treatments of step (c) are repeated up to five times.

10. A process for manufacturing a case hardened stainless steel high performance component comprising the steps of:

(a) providing a component made from an alloy composition including in % by weight 0.10 to 0.25 C, 1 max Mn, 1 max Si, 13 to 19 Cr, 3 to 5 Mo, 0.25 to 1.25 V, 1.75 to 5.25 Ni, 5 to 14 Co, 0.01 to 0.10 Nb, 0.02 max B, balance Fe and incidental impurities;

(b) case hardening by one of carburizing or carbonitriding the component to achieve a carbon plus nitrogen content of at least 1.5 wt.% in a case defining a working surface of the component;
(c) austenitizing the carburized component at about 1950° to 2100°F
(1066° to 1149°C);
(d) quenching the austenitized component;
(e) sub-zero cooling the component to at least -110°F (-79°C) or lower;
(f) stress relieving tempering the component at about 400° to 500°F
(204° to 260°C);
(g) deep cryogenically treating the component at about -120° to
-321°F (-84° to -196°C) for at least one hour; and
(h) re-warming the component to room temperature and tempering at
about 600° to 1100°F (316° to 593°C) for at least two hours.

11. The process of claim 10 wherein steps (g) and (h) are repeated at least one time.

12. The process of claim 10 wherein the high performance component is a bearing element.

13. The process of claim 10 wherein the high performance component is a gear.

14. The process of claim 10 wherein the high performance component is a fastener.

15. The process of claim 10 wherein the carburizing step (b) is carried out in a plasma assisted vacuum furnace.

16. A high performance component having a core, a case and an intermediate layer between the core and the case, wherein the case is harder than the
core and the intermediate layer is softer than the core, said core comprising Fe, 0.05 to 0.50 wt.% C and at least 11 wt.% Cr and having a predominantly martensitic microstructure, wherein the intermediate layer consists substantially entirely of an austenitic microstructure, and wherein the case contains at least 1.5 wt.% carbon plus nitrogen and consists of a predominantly martensitic matrix containing a large volume fraction of fine, spherical alloy carbides having a high hardness and fatigue resistance.

17. The high performance component of claim 16 manufactured from an alloy comprising in % by weight 0.10 to 0.25 C, 1 max Mn, 1 max Si, 13 to 19 Cr, 3 to 5 Mo, 0.25 to 1.25 V, 1.75 to 5.25 Ni, 5 to 14 Co, 0.01 to 0.10 Nb, 0.02 max B, balance Fe and incidental impurities.

18. The high performance component of claim 17 comprising one of a bearing element, cam, gear or fastener.

19. The high performance component of claim 16 wherein the carbon plus nitrogen content in the case is about 2 wt.% to about 2.5 wt.%.

20. The high performance component of claim 16 wherein the carbon plus nitrogen content in the case is at least 2.5 wt.%.
**FIG. 1**

Diagram showing hardness variations with depth. The graph plots depth (mm) on the x-axis and hardness (HRC) on the y-axis. Markings indicate different hardness levels at specific depths:
- 1.52 mm (0.060 in) = 77.5 HRC
- 0.38 mm (0.015 in) = 67 HRC
- Core = 50 HRC