

METAL ARTICLE WITH HIGH INTERSTITIAL CONTENT

Cross-Reference to Related Application

[0001] This application is based on, and claims priority to, prior U.S. Provisional Patent Application Serial No. 60/832,844, filed July 24, 2006, the disclosure of which is incorporated herein by reference.

Background

[0002] Case hardening is a widely used industrial process for enhancing the surface hardness of shaped metal articles. In a typical commercial process, the workpiece is contacted with natural gas or propane at elevated temperature whereby carbon atoms liberated by decomposition of the carbon compound diffuse into the workpiece's surface. Hardening occurs through the reaction of these diffused carbon atoms with one or more metals in the workpiece thereby forming distinct chemical compounds, i.e. carbides, followed by precipitation of these carbides as discrete, extremely hard, crystalline particles in the metal forming the workpiece's surface. See, Stickels, "Gas Carburizing", pp 312 to 324, Volume 4, *ASM Handbook*, © 1991, ASM International.

[0003] Carbide precipitates not only enhance surface hardness, they can also promote corrosion. For this reason, stainless steel is rarely case hardened by conventional gas carburization, since the corrosion resistance of the steel is compromised.

[0004] In the mid 1980's, a technique for case hardening stainless steel was developed in which the workpiece is contacted with carbon monoxide and hydrogen at low temperature, typically below 500° C (932° F). At these temperatures, and provided that carburization does not last too long, carbon atoms liberated by decomposition of the carbon monoxide diffuse into the workpiece surfaces, typically to a depth of 20-50 μ , without formation of carbide precipitates. Nonetheless, an extraordinarily hard case (surface layer) is obtained, which is believed due to the stress placed on the crystal lattice of the metal by the diffused carbon atoms. Moreover, because carbide precipitates are absent, the corrosion resistance of the steel is unimpaired, even improved.

[0005] This technique, which is referred to a "low temperature carburization," is described in a number of publications including U.S. 5,556,483, U.S. 5,593,510, U.S. 5,792,282, U.S. 6,165,597, U.S. 6,547,888, EPO 0787817, Japan 9-14019 (Kokai 9-268364) and Japan 9-71853 (Kokai 9-71853). The disclosures of these documents are incorporated herein by reference.

Summary of the Invention

[0006] In accordance with this invention, very thin workpieces are low temperature carburized so that diffused carbon reaches a substantial portion of the product's core. The result is that new products are obtained which, as a whole, contain higher levels of interstitial (diffused) carbon and exhibit better combinations of properties than seen in the past.

[0007] Thus, this invention provides a process for producing a thin metal product in which at least one property of the thin metal product, as a whole, is enhanced by at least 10% as compared with an otherwise identical untreated product, the process comprising subjecting a thin metal workpiece to a low temperature diffusion-based surface treatment, preferably low temperature carburization. Most commonly, yield strength is substantially increased while ductility is substantially retained.

[0008] In addition, this invention also provides a thin metal product produced by subjecting a thin metal workpiece to a low temperature diffusion-based surface treatment, the thin metal product as a whole exhibiting at least one property which is enhanced by at least 10% as compared with an otherwise identical product not subjected to such surface treatment, preferably low temperature carburization.

[0009] Finally, this invention also provides a shaped article which is produced by forming a mass of the thin metal product described above into a desired shape and sintering.

Brief Description of the Drawings

[0010] The present invention may be more readily understood by reference to the drawings wherein:

[0011] Figs. 1 and 2 show the effect on the yield strength and ductility of AISI 316 stainless steel foil low temperature carburized in accordance with this invention, Fig. 1 illustrating

the raw load vs. displacement data and Fig. 2 showing the data normalized to a standard stress/strain curve.

Low Temperature Carburization

[0012] As indicated above, the primary focus of this invention is on the low temperature carburization of iron-, nickel-, cobalt-, and/or chromium-based alloys, especially stainless steel. In this process, which is extensively described in the above-noted U.S. 5,556,483, U.S. 5,593,510, U.S. 5,792,282, U.S. 6,165,597, U.S. 6,547,888, EPO 0787817, Japan 9-14019 (Kokai 9-268364) and Japan 9-71853 (Kokai 9-71853), elemental carbon diffuses into the metal matrix forming the workpiece without formation of carbide precipitates. In this context, reference to carburizing stainless steel “without formation of carbide precipitates” will be understood to mean “without formation of the types and amounts of carbide precipitates which adversely affect the corrosion resistance of the stainless steel.”

[0013] In accordance with the present invention, low temperature carburization is carried out in the same way as done in the past so as to produced carburized workpieces whose treated surfaces or “case” contain elevated amounts of elemental carbon, normally about 2-15 atomic %, more typically about 5-10 atomic % or even 9-12 atomic %. Because low temperature carburization is a diffusion-based process, the concentration of carbon in the workpiece’s surface decreases from a maximum at or very near the outermost surface of the workpiece down to an equilibrium value (which is the carbon concentration in the “native” or untreated metal from which the workpiece is made) in accordance with Fick’s law. Thus, it will be understood that reference to a carbon concentration of about 2-15 atomic % means that this is the carbon concentration at or near the workpieces surface, with this concentration falling off to the equilibrium value at depth which can be as little as 5 μ from the workpiece’s outer surface, but is more typically on the order of 20-50 μ from the workpiece’s outer surface. Greater depths of diffused carbon, e.g., as deep as 75 μ or even 100 μ are possible, however.

Other Low Temperature Diffusion-Based Surface Treatments

[0014] Although this invention concentrates on low temperature carburization of iron-, nickel- and cobalt-based alloys, other analogous diffusion-based surface treatments can also be used.

[0015] In low temperature carburization, as indicated above, atomic carbon diffuses interstitially into the workpiece surfaces, i.e., carbon atoms travel through the spaces between the metal atoms without significant substitutional diffusion of the metal atoms. Because the processing temperature is low, these carbon atoms form a solid solution with the metal atoms of the workpiece surfaces. They do not react with these metal atoms to form other compounds. Low temperature carburization is therefore different from normal carburization carried out at higher temperatures in which the carbon atoms react to form corrosion-promoting carbide precipitates, i.e., specific metal compounds such as $M_{23}C_6$ (e.g., $Cr_{23}C_6$ or chromium carbide), M_5C_2 and the like, arranged in the form of discrete phases separate and apart from the metal matrix in which they are contained.

[0016] Other analogous processes are known for altering the surface characteristics of a metal workpiece by interstitial diffusion of atoms into the workpiece surfaces at relatively low temperatures to form solid solutions with the metal atoms therein without formation of new compounds in separate phases. Examples include nitriding of iron, chromium and/or nickel based alloys, carbo-nitriding of iron, chromium and/or nickel based alloys, and nitriding of titanium-based alloys, to name a few. For convenience, all of these processes will be referred to collectively as "low temperature interstitial diffusion based surface treatments."

[0017] All such low temperature interstitial diffusion-based surface treatments can be used in accordance with the present invention. That is to say, each of these low temperature interstitial diffusion-based surface treatments can be applied to thin metal workpieces using the technology of this invention to make new products with greater concentrations of the diffused atoms and better properties than available in the past.

Alloys

[0018] The present invention will normally be carried on workpieces made from iron or nickel-based alloys. Such materials are well known and described for example in the above-noted US Patent No. 5,792,282, U.S. Patent No. 6,093,303, U.S. Patent No. 6,547,888, EPO 0787817 and Japanese Patent Document 9-14019 (Kokai 9-268364).

[0019] Particular alloys of interest are steels, especially steels containing 5 to 50, preferably 10 to 40, wt.% Ni. Preferred alloys contain 10 to 40 wt.% Ni and 10 to 35 wt.% Cr. More preferred are the stainless steels, especially the AISI 300 series steels. Of special interest are

AISI 301, 303, 304, 309, 310, 316, 316L, 317, 317L, 321, 347, CF8M, CF3M, 254SMO, A286 and AL6XN stainless steels. As of this writing, the invention has not been successfully practiced on 400 series stainless steels, which is believed due to the fact that appropriate conditions for depassivating the steel in preparation for low temperature carburization have not yet been determined. Nonetheless, the AISI 400 series stainless steels and especially Alloy 410, Alloy 416 and Alloy 440C are also of special interest.

[0020] Particular nickel-based alloys which can be low temperature carburized in accordance with this invention include Alloy 600, Alloy 625, Alloy 825, Alloy C-22, Alloy C-276, Alloy 20 Cb and Alloy 718, to name a few examples.

[0021] In addition to iron- and nickel-based alloys, low temperature carburization in accordance with the present invention can also be practiced on cobalt-based alloys as well as manganese-based alloys. Examples of such cobalt-based alloys include MP35N and Biodur CMM, while examples of such manganese-based alloys include AISI 201, AISI 203EZ and Biodur 108.

[0022] The particular phase of the metal being processed in accordance with the present invention is unimportant, as the invention can be practiced on metals of any phase structure including, but not limited to, austenite, ferrite, martensite, duplex metals (e.g., austenite/ferrite), etc.

Thin Workpieces and Products

[0023] In accordance with the present invention, a low temperature interstitial diffusion-based surface treatment is carried out on a "thin" workpiece to produce a "thin" surface-treated product.

[0024] A workpiece that has been subjected to a low temperature interstitial diffusion-based surface treatment can be considered as having an internal core surrounded by a diffusion-enriched surface or "case". When the interstitial diffusion treatment is low temperature carburization, this carburized surface will normally extend down to a depth of about 20 μ to about 40 μ or even 50 μ from the outermost surface, although greater depths are possible. Because this case depth is extremely thin compared with the overall thickness of the workpiece, the vast majority and indeed essentially all of the article is composed of native metal i.e., metal not infused with additional amounts of interstitial carbon. As a result, the case exerts no noticeable effect on the mechanical properties of the workpiece as a whole.

[0025] In accordance with the invention, however, the workpiece being processed is very thin, normally on the order of 0.0004 to 0.01 inch thick (~ 0.01 to ~ 0.25 mm; ~ 10 to ~ 250 μ), more typically about 0.001 to 0.003 inch thick (~ 0.025 to ~ 0.08 mm; ~ 25 to ~ 75 μ). At these small workpiece thicknesses, case thickness becomes significant relative to core thickness, the result of which is that the properties of the workpiece as a whole are indeed influenced by the case. Thus it is possible, in accordance with the present invention, to produce new materials having properties not previously seen before.

[0026] This is illustrated in the Figs. 1 and 2 which shows the stress/strain relationships exhibit by a number of different AISI 316 stainless steel foils 0.002 in (~ 0.048 mm; ~ 50 μ) thick which have been low temperature carburized to produce a "thin" surface-treated foil product in accordance with the present invention. As can be seen from this figure, the untreated foil represented by Curve A reached its elastic limit at a stress of about 300 MPa (megaPascals). In contrast the foils treated in accordance with the present invention, which are represented by Curve B, did not reach their elastic limits until the applied stress was about 1200 MPa. This represents a four-fold increase in yield strength with ductility being substantially retained, thereby showing that these treated foils are considerably different materials from the untreated foils from which they were made.

[0027] As indicated above, the workpieces processed by the present invention are thin, normally on the order of 0.0004 to 0.01 inch thick (~ 0.01 to ~ 0.25 mm; ~ 10 to ~ 250 μ), more typically about 0.001 to 0.003 inch thick (~ 0.024 to ~ 0.08 mm; ~ 25 to ~ 75 μ). However, workpieces of greater or lesser thickness can also be processed if desired. What is important is that these workpieces are thin enough, and the low temperature diffusion-based surface treatment carried out long enough, so that the case produced by this surface treatment imparts a not-insignificant change (i.e. $\geq 10\%$) to at least one property of the product as a whole as compared with an otherwise identical workpiece from which it is made.

[0028] So in the context of this disclosure, "thin" in relation to a workpiece which is subjected to a low temperature interstitial diffusion surface treatment will be understood to mean a thickness which is small enough so that at least one property of the product produced by the treatment is enhanced by at least 10% as compared with an otherwise identical product made without the surface treatment.

[0029] Particular examples of “thin” workpieces and products for the purposes of this invention include foils, wires, powder, platelets and other particulates, for example. Other shapes are also possible.

Property Enhancements

[0030] Various different mechanical, electrical and magnetic properties of thin metal workpieces can be enhanced by this invention. Examples include, but are not limited to hardness, yield strength, ultimate tensile strength, elastic limit, electrical resistance and magnetic susceptibility. Moreover, while the above disclosure refers to enhancing at least one of these properties by at least 10%, it should be appreciated that far greater enhancements are possible. For example, electrical resistance can be increased by as much as 20%, 30%, 40%, 50%, 60%, 70%, 80%, 90% or even 100%, typically 15% to 60%. Similarly, yield strength increases by as much as 100%, 200%, 300%, 400% and even 500% are possible. Most significantly, these remarkable enhancement can be achieved without significant reduction in other properties such ductility, etc., as a practical matter.

[0031] This is further illustrated in the Figs. 1 and 2 which shows that the foils low temperature carburized in accordance with this invention, Curve B, remained ductile until they ruptured at an elongation of about 20% or more. Although this elongation at rupture is not as great as that exhibited by the untreated foils of Curve A (about 35% elongation at rupture), it is far greater than that of the conventionally carburized foils (about 5% elongation at rupture), represented by Curve C. Thus the present invention not only achieves a substantial increase in yield strength, electrical resistance and corrosion resistance, but also does so without substantial sacrifice in ductility.

Sintered Articles

[0032] In accordance with another feature of this invention, shaped metal articles are made by sintering processes using masses of the diffusion-treated thin metal products of this invention as their raw materials. Powder metallurgy techniques for forming shaped metal articles are well known, and any such technique can be used to form shaped metal articles from the diffusion-treated powders, platelets and other particulate thin products of this invention. Analogous sintering processes can also be used to form the thin metal foil products of this invention into shaped articles.

[0033] Such sintering processes typically involve forming a mass of metallic particles into a desired shape, optionally compacting the mass to desired density (with respect to theoretical) and heating the mass to cause the particles to melt and fuse to one another at their surfaces. Analogous sintering processes can be used to form shaped metal articles from foils. These same processes can be used to form shaped articles of any desired shape from the diffusion-treated thin metal products of this invention regardless of shape, i.e., whether in the form of powder, platelet, other particulate, wire or foil. Such products are unique because they are made from new materials not previously known.

Magnetic Susceptibility

[0034] Another feature of the thin metal products of this invention when made from austenitic stainless steels, including shaped metal articles made by sintering masses of such thin metal products, is that they exhibit significant magnetic susceptibility. Magnetic susceptibility is the degree of magnetization of a material in response to an applied magnetic field. The dimensionless volume magnetic susceptibility, represented by the symbol χ_v (also represented in the literature by κ or K), is defined by the relationship

$$\mathbf{M} = \chi_v \mathbf{H}$$

where

$\mathbf{M}$ is the magnetization of the material (the magnetic dipole moment per unit volume), measured in amperes per meter, and

$\mathbf{H}$ is the applied field, also measured in amperes per meter.

[0035] Ferritic and martensitic stainless steels exhibit good, inherent magnetic susceptibility. In contrast, austenitic stainless steels exhibit essentially no magnetic susceptibility. However, the carbon hardened surfaces produced when austenitic stainless steels and other metals having face centered cubic lattice structures are low temperature carburized do. Accordingly, when a "thin" workpiece made from an austenitic stainless steel or other metal having a face centered cubic lattice structure is low temperature carburized, the "thin" product obtained exhibits significant magnetic susceptibility since its carbon hardened surfaces represent a significant portion of its entire mass. In the same way, a shaped metal article made from a sintered mass of such a product, as described above, also exhibits significant magnetic susceptibility as a whole since the portion of its mass which has been low temperature carburized is significant with respect to its entire mass.

[0036] Although only a few embodiments of this technology have been described above, it should be appreciated that many modifications can be made. All such modifications are intended to be included within the scope of this disclosure, which is to be limited only by the following claims.

Claims

1. The process comprising subjecting a thin metal workpiece to a low temperature interstitial diffusion-based surface treatment to produce a thin metal product in which at least one property of the thin metal product, as a whole, is enhanced by at least 10% as compared with an otherwise identical product not subjected to such surface treatment.
2. The process of claim 1, wherein the property being enhanced is at least one of hardness, yield strength, ultimate tensile strength, elastic limit, electrical resistance and magnetic susceptibility.
3. The process of any one of the preceding claims, wherein the thin metal workpiece is about 0.01 to 0.25 mm thick.
4. The process of any one of the preceding claims, wherein the metal workpiece is a wire, powder, platelet, other particulate or foil.
5. The process of any one of the preceding claims, wherein the low temperature diffusion-based surface treatment is low temperature carburization.
6. The process of any one of the preceding claims wherein the metal is an iron-, nickel-, cobalt-based or manganese-based alloy.
7. The process of claim 6, wherein the metal is stainless steel.
8. A thin metal product produced by subjecting a thin metal workpiece to a low temperature diffusion-based surface treatment, the thin metal product as a whole exhibiting at least one property which is enhanced by at least 10% as compared with an otherwise identical product not subjected to such surface treatment.
9. The thin metal product of claim 8, wherein the thin metal product is produced by subjecting a thin metal workpiece made from an iron-, nickel- or cobalt-based or manganese-based alloy to low temperature carburization.
10. The thin metal product of claim 9, wherein the thin metal product has a yield strength at least 100% greater than an otherwise identical product not subjected to low temperature carburization, the thin metal product exhibiting a ductility in terms of elongation at fracture of at least 20%.

11. The thin metal product of any one of claims 8 to 10, wherein the thin metal product is a powder.
12. A shaped article produced by forming a mass of the thin metal product of claim 1 into a desired shape and sintering.
13. The shaped article of claim 12, wherein the thin metal product is produced by subjecting a thin metal workpiece made from an iron-, nickel- or cobalt-based or manganese-based alloy to low temperature carburization.
14. The shaped article of claims 12 or 13, wherein the thin metal product is a powder.
15. A process for forming a shaped metal article by powder metallurgy techniques in which a mass of metallic particles is formed into a desired shape, optionally compacted into a desired density and heated to cause the particles to melt and fuse to one another at their surfaces, CHARACTERIZED IN THAT the metallic particles are made from an iron-, nickel-, cobalt- or manganese-based alloy that has been subjected to low temperature carburization in an amount sufficient to enhance at least one of the hardness, yield strength, ultimate tensile strength, elastic limit, electrical resistance and magnetic susceptibility of the alloy by at least 10%.
16. The thin metal product of claim 8, wherein the thin metal product is a carburized thin metal foil product made from an AISI 300 series stainless steel having a thickness of about 10 to 250 microns and being produced by subjecting a thin metal foil to low temperature carburization without formation of carbide precipitates, the carburized thin metal foil product as a whole having a yield strength at least 10% greater than an otherwise identical thin metal foil not subjected to low temperature carburization.
17. The thin metal product of claim 16, wherein the thin metal workpiece is about 24 to 80 microns thick.
18. The thin metal product of claim 17, wherein the thin metal workpiece is made from an AISI 316 or 316L stainless steel.
19. The thin metal product of claim 16, wherein the thin metal workpiece is made from an AISI 316 or 316L stainless steel.

20. The thin metal product of claim 19, wherein the thin metal workpiece has a yield strength at least 100% greater than an otherwise identical product not subjected to low temperature carburization.

21. The thin metal product of claim 20, wherein the thin metal workpiece has a yield strength at least 200% greater than an otherwise identical product not subjected to low temperature carburization and a ductility in terms of elongation at fracture of at least 20%.

22. The thin metal product of claim 16, wherein the thin metal workpiece has a yield strength at least 100% greater than an otherwise identical product not subjected to low temperature carburization.

23. The thin metal product of claim 22, wherein the thin metal workpiece has a yield strength at least 200% greater than an otherwise identical product not subjected to low temperature carburization and a ductility in terms of elongation at fracture of at least 20%.

24. The thin metal product of claim 8, wherein the thin metal product is a surface-modified thin metal foil product made from an iron-, nickel- or cobalt-based alloy having a thickness of about 10 to 250 microns and being produced by subjecting a thin metal foil to a low temperature interstitial diffusion based surface treatment without formation of new compounds in separate phases, the surface-modified thin metal foil product as a whole having at least one property selected from yield strength, ultimate tensile strength, elastic limit, electrical resistance and magnetic susceptibility which is enhanced by at least 10% as compared with an otherwise identical thin metal foil not subjected to such low temperature interstitial diffusion based surface treatment.

25. The thin metal product of claim 24, wherein the thin metal workpiece is about 24 to 80 microns thick.

26. The thin metal product of claim 24, wherein the thin metal workpiece is made from

- (a) a stainless steel selected from AISI 301, 303, 304, 309, 310, 317, 317L, 321, 347, CF8M, CF3M, 254SMO, A286, AL6XN, 410, 416 and 440C stainless steels,
- (b) a nickel-based selected from Alloy 600, Alloy 625, Alloy 825, Alloy C-22, Alloy C-276, Alloy 20 Cb and Alloy 718,

- (c) a cobalt-based alloy selected from MP35N and Biodur CMM, and
- (d) a manganese-based alloy selected from AISI 201, AISI 203EZ and Biodur 108.

27. The thin metal product of claim of claim 26, wherein the thin metal workpiece is about 24 to 80 microns thick.

28. The shaped article of claim 12, wherein the shaped article is a shaped article made from an austenitic stainless steel produced by forming a mass of carburized metal powder into a desired shape and sintering, the shaped article having a magnetic susceptibility at least 10% greater than an otherwise identical shaped article made from a mass of otherwise identical metal powder which has not been carburized,

the carburized metal powder being made by subjecting metal powder made from an austenitic stainless steel and having a thickness of about 10 to 250 microns to low temperature carburization without formation of carbide precipitates.