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(54) ION-IMPLANTED ELECTROFORMED STRUCTURAL MATERIAL AND METHOD OF PRODUCING THE STRUCTURAL MATERIAL

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(57) **ABSTRACT**

An ion-implanted electroformed structural material is made of an electroformed body formed by electroforming and has an ion-implanted layer formed by implanting ions into the electroformed body. In the electroformed structural material, the microstructure is modulated at a position deeper than the ion-implanted layer, and the hardness becomes higher than that of the original electroformed body even at a position deeper than the ion-implanted layer.

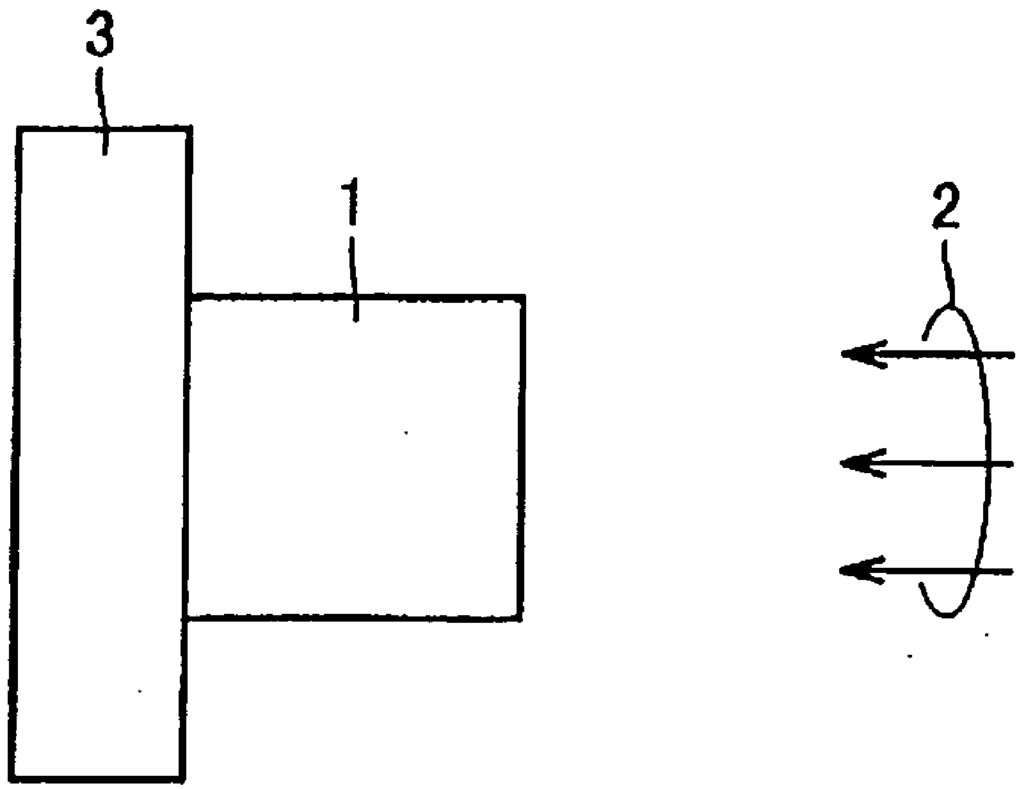


FIG. 1

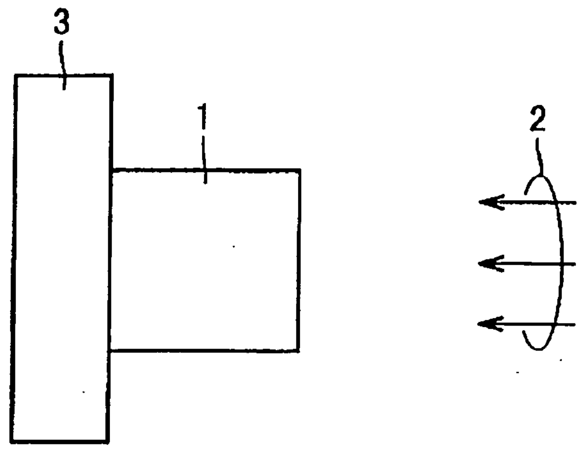


FIG. 2

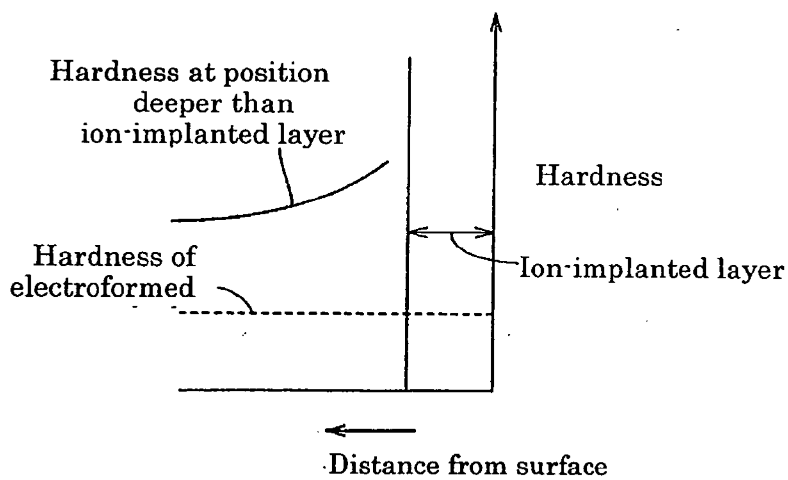


FIG. 3

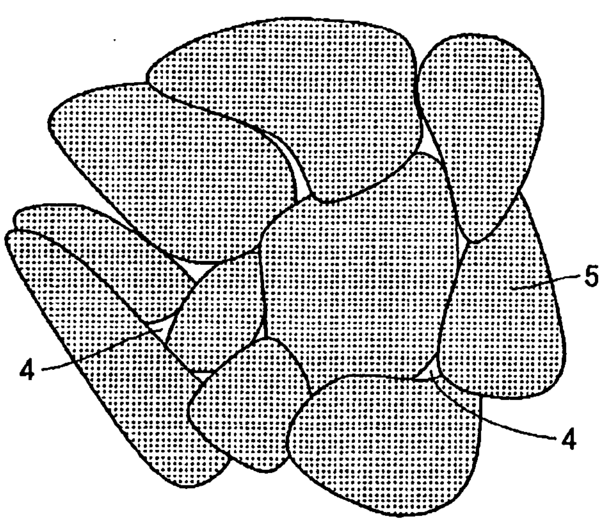


FIG. 4

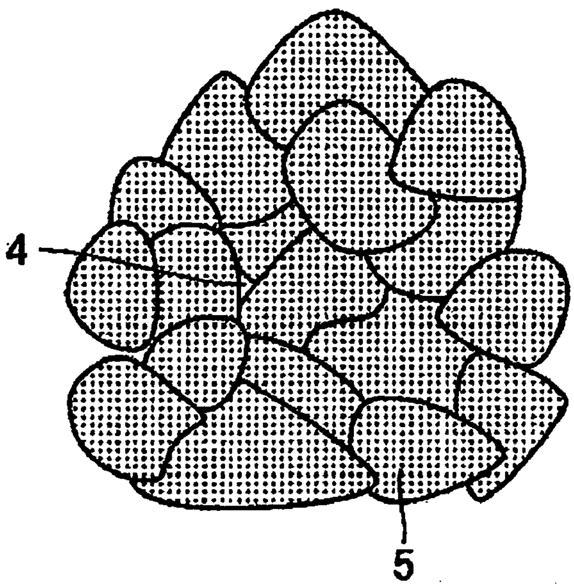


FIG. 6

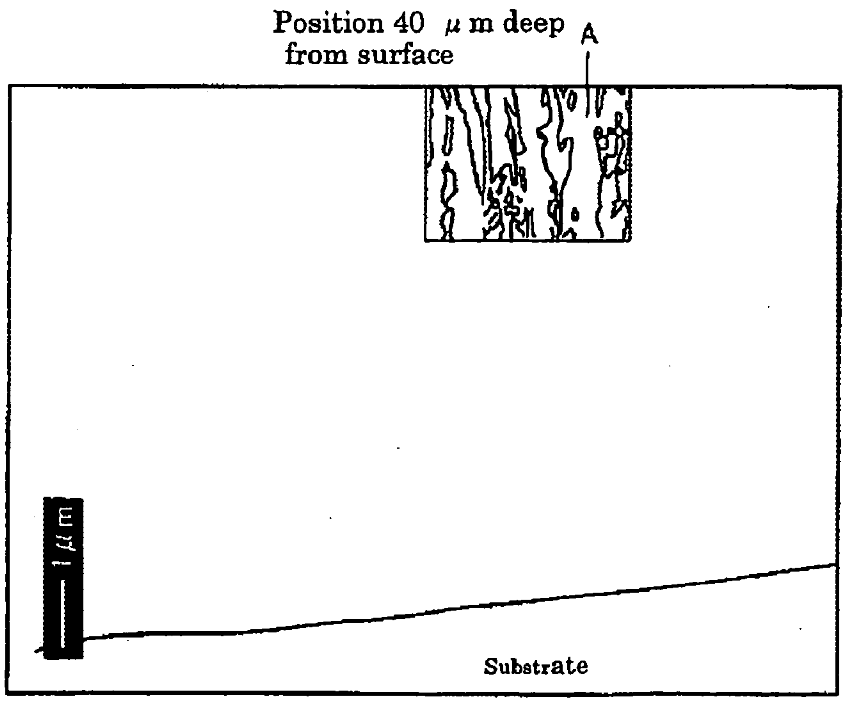


FIG. 5

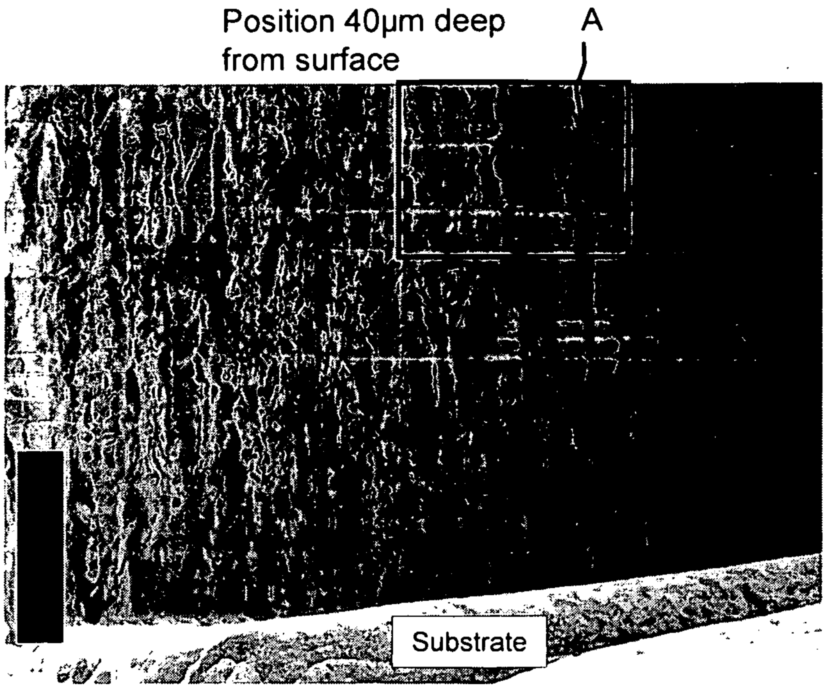

Position 40μm deep
from surface
A
Substrate

FIG. 7

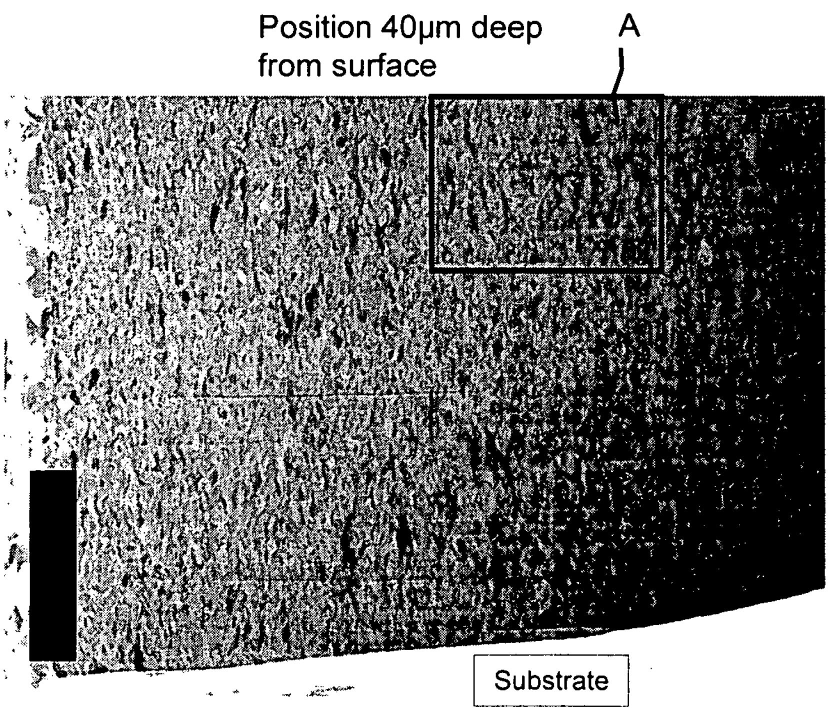
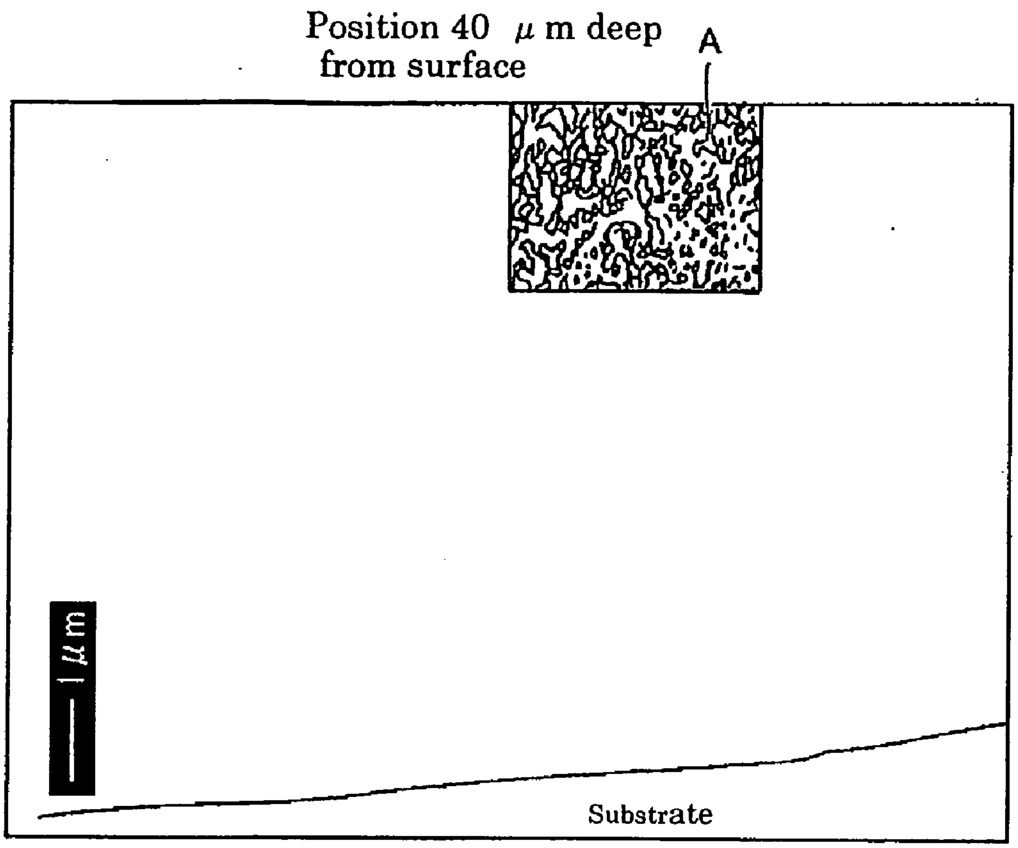

Position 40μm deep
from surface
A
Substrate

FIG. 8



ION-IMPLANTED ELECTROFORMED STRUCTURAL MATERIAL AND METHOD OF PRODUCING THE STRUCTURAL MATERIAL

BACKGROUND OF THE INVENTION

[0001] 1. Field of the Invention

[0002] The present invention relates to an ion-implanted electroformed structural material and a method of producing the structural material, and more specifically to an ion-implanted electroformed structural material made of an electroformed body in which a portion deeper than an ion-implanted layer at the surface portion has an increased hardness and a method of producing the structural material.

[0003] 2. Description of the Background Art

[0004] The LIGA process is useful for producing high-precision metallic microstructural bodies on a mass-production basis (LIGA is the abbreviation of Lithographie (lithography) Galvanoformung (electroforming) Abformung (molding)). The LIGA process uses synchrotron radiation (SR), which is an X-ray having high directivity. Consequently, the LIGA process can perform deep lithography. More specifically, it can process a structural body having a height of several hundreds of micrometers with a precision on the order of micrometers. In other words, it can easily produce a metallic microstructural body having a large thickness. It also has other special features. Therefore, the LIGA process is expected to be applied to a wide range of fields.

[0005] The LIGA process is a processing technique that combines lithography, plating as electroforming, and molding. In the LIGA process, for example, a resist layer formed on an electrically conductive substrate is irradiated with SR through an absorbing mask (reticle) having a predetermined pattern. This lithography forms a resist structured body (resin mold) in accordance with the pattern of the absorbing mask (mask pattern). When metal is deposited in the opening of the mask pattern with electroforming, a metallic microstructured body can be obtained. When this high-precision metallic microstructured body is used as a molding die, a microstructured mold body made of synthetic resin can be produced with injection molding or the like. When thus obtained microstructured mold bodies are combined, a micromachine can be produced. The above-described technique is described, for example, in a paper reported by Manabu Yasui, Yasuo Hirahayashi, and Hiroyuki Fujita (pp. 734-737, No. 11, Vol. 52, 2001, "*Journal of the Surface Finishing Society of Japan*").

[0006] However, in the above-described LIGA process, the metal to be formed with the electroforming treatment is limited to the metal that can be plated, such as nickel (Ni), iron (Fe), cobalt (Co), and Ni—Fe alloy. When a higher hardness or a higher strength is required, a high-hardness material, such as Ni-manganese (Mn) alloy or Ni-tungsten (W) alloy, has sometimes been used. In this case, however, a highly advanced technique is required for the control of the plating solution and the like. This requirement limits the range of its applications.

[0007] In addition, when the wear resistance is required to a microstructured part, its surface can be provided with a hard coating formed by a process such as plating, physical vapor deposition (PVD), or chemical vapor deposition (CVD). In this case, however, how to achieve the sufficient bonding strength between the part body and the coating poses a problem. Furthermore, when the shape is complicated, it may be difficult to form a coating at a shaded portion at the time of the vapor deposition and at a minutely concaved portion.

[0008] On the other hand, when electroforming is performed by using a fused salt, in place of aqueous solution, as the electroforming bath, this process can produce a highly hard electroformed body made of chromium (Cr), titanium (Ti), molybdenum (Mo), or the like in comparison with the conventional Ni-based alloy. However, the fused salt applicable to the electroforming using the above-described metals is limited to a temperature of 250° C. or more. Consequently, in the lithography using the ordinary photoresist, the resist deforms due to the heat, rendering itself unusable. In addition, fused salts are highly moisture absorptive and chemically reactive. The properties pose limitations such as the requirement of performing the electroforming in an inert-gas environment.

[0009] In view of the above-described circumstances, the industry has been requiring to develop an electroformed structural material that can be formed with an ordinary method and that can be easily improved in strength and a method of producing the structural material.

SUMMARY OF THE INVENTION

[0010] An object of the present invention is to offer an ion-implanted electroformed structural material that can easily improve the strength of an electroformed body and a method of producing the structural material.

[0011] According to the present invention, the foregoing object is attained by offering the following ion-implanted electroformed structural material. The ion-implanted electroformed structural material is made of an electroformed body formed by electroforming. The electroformed structural material has an ion-implanted layer formed by implanting accelerated ions into the electroformed body.

[0012] In the electroformed structural material, an ion-implanted layer having high strength is formed at the surface portion, and a modulated structure having a finer structure is formed at a position deeper than the ion-implanted layer. As a result, the strength can be improved at the surface portion and a portion deeper than the surface portion.

[0013] According to one aspect of the present invention, the present invention offers the following method of producing an ion-implanted electroformed structural material. The method comprises (a) a step of forming an electroformed body and (b) a step of implanting accelerated ions into the electroformed body. The combination of the foregoing steps enables the formation of the modulated structure having a finer structure at a position deeper than the ion-implanted layer at the surface portion.

[0014] According to the present invention, when the ion-implanted electroformed structural material and the method of producing the structural material are used, the durability of an electroformed structural material can be easily improved. Therefore, the structural material and the method can be used for electroformed structural materials in general that have so far required to perform forging to improve the strength as well as minute electroformed structural materials for micromachines. Consequently, the technique developed by the present invention is expected to be employed in a wide range of applications including the elimination of the forging process and other unknown uses.

BRIEF DESCRIPTION OF THE DRAWING

[0015] In the drawing:

[0016] FIG. **1** is a diagram explaining the method of producing the ion-implanted electroformed structural material, which is an embodiment of the present invention.

[0017] FIG. **2** is a graph showing a depthwise distribution of the hardness of the ion-implanted electroformed structural material of the present invention.

[0018] FIG. **3** is a schematic diagram showing the microstructure of a material as electroformed.

[0019] FIG. **4** is a schematic diagram showing the microstructure of an electroformed body after the ion implantation.

[0020] FIG. **5** is a view showing a focused ion beam (FIB) photograph taken at a position 40 μm deep from the surface of a material as electroformed.

[0021] FIG. **6** is a line drawing showing the microstructure of the portion "A" shown in FIG. **5**.

[0022] FIG. **7** is a view showing an FIB photograph taken at a position 40 μm deep from the surface of the electroformed body after it is ion-implanted.

[0023] FIG. **8** is a line drawing showing the microstructure of the portion "A" shown in FIG. **7**.

DETAILED DESCRIPTION OF THE INVENTION

[0024] The present inventors found a phenomenon that when ions are implanted into an electroformed body, the implantation increases the hardness at a portion beyond the reach of the ions. However, the mechanism of the generation of the phenomenon is yet to be clarified. The present inventors studied various literatures, but were not able to confirm the fact that the above-described phenomenon was publicized. Nevertheless, experiments conducted by varying the experimental conditions confirmed the reproducibility of the phenomenon.

[0025] Embodiments of the present invention are explained below by referring to the drawing. FIG. **1** is a diagram explaining the method of producing the ion-implanted electroformed structural material in an embodiment of the present invention. An electroformed body **1** is formed on a metallic substrate **3** in accordance with the pattern of a rest layer (not shown). Ions **2** are driven into the electroformed body **1** with an accelerating voltage of 10 kV or more, so that they are implanted. This ion implantation increases the hardness at a portion deeper than the ion-implanted layer as shown in FIG. **2**. The increase in hardness from that of an untreated body is 30% in most cases and as large as 50% in some instances. This increase is conspicuous. The ion-implanted layer is formed in a region 5 μm or less in depth. FIG. **2** does not indicate the hardness in the region of the ion-implanted layer.

[0026] FIG. **3** is a schematic diagram showing the microstructure of an electroformed body. It is possible to obtain a fine structure even in an electroformed body. More specifically, when electroforming is performed by applying a pulse-shaped voltage across the electrodes in the electroforming bath to supply a pulse-shaped current, the density of the nucleation sites for the deposition increases at the time of the deposition of the electroformed body from the electroforming solution. As a result, an electroformed body having a fine structure can be obtained. The schematic diagram in FIG. **3** shows an electroformed body having such a fine structure. In the case of an electroformed body, the crystal grows continuously from the surface of the electrode. Consequently, sometimes, columnar crystals long in the growth direction are formed, which is typical of cast metal. Sometimes, equiaxed crystals are formed, which has no orientation. The schematic diagram in FIG. **3** may be interpreted as a diagram showing either the equiaxed crystals or the cross section of the columnar crystals. In the case of the columnar crystals, the average grain diameter is a grain diameter measured in a longitudinal section.

[0027] There are voids **4** (also known as cavities or pores), which are typical of the electroformed body, between fine crystal grains **5** in the crystal structure shown in FIG. **3**. On the other hand, FIG. **4** shows a modulated structure, which has a finer structure, at a portion deeper than the ion-implanted layer. As shown in FIG. **4**, the crystal grains **5** become finer than the crystal grains as electroformed. Accordingly, it appears that the voids **4** become smaller. The imperfections (defects) such as voids seem to be partially consumed into the increment of the grain boundaries, which are a type of imperfection (defect), when the crystal grains become finer. However, as described above, this is probably a phenomenon that is first encountered in the very long history of the bulk metal material. Therefore, the present inventors refrain from making a clear affirmation. The above description is to be understood as only a description of the fact the present inventors notice.

[0028] FIG. **5** is a view showing a focused ion beam (FIB) photograph of an electroformed body. FIG. **6** is a line drawing showing the structure of the portion "A" shown in FIG. **5**. The electroformed body is formed as columnar crystals, and the columnar crystals have an average grain diameter of less than 1 μm. Although the electroformed body contains voids, they cannot be observed in FIG. **5** due to the insufficient magnification.

[0029] FIG. **7** is a view showing an FIB photograph showing the structure after ions are implanted from the surface side of the above-described electroformed body. FIG. **8** is a line drawing showing the portion "A" corresponding to the portion "A" shown in FIG. **5**. The comparison between the line drawings in FIGS. **6** and **8** shows that the structure is modulated and becomes finer at a position in the interior 40 μm away from the surface, that is, at the interior the ions do not reach. As can be observed in FIG. **8**, the way of modulation seems to be affected by the original columnar crystals. More specifically, the structure appears to become finer with maintaining slightly slender shapes along the longitudinal axis of the columnar crystals. The degree of becoming finer is noticeable, and the average crystal-grain diameter appears to be much smaller than 0.5 μm.

[0030] As described above, it is probable that the above-described increase in hardness can be achieved by the formation of the modulated structure, which has a finer structure, at a position deeper than the ion-implanted layer.

EMBODIMENT

[0031] Plating (electroforming) was performed for 100 minutes at a temperature of 55° C., at a current of 5 A, with the following composition of a plating bath (electroforming bath), and by using an nickel plate having a size of 10-cm square as the cathode and nickel as the anode:

[0032] {Plating Bath}

[0033] Nickel sulfamate: 300 g/l (g/dm^3)

[0034] Manganese sulfamate: 40 g/l

[0035] First brightener (sodium saccharic acid): proper amount

[0036] Second brightener (butynediol): proper amount

[0037] Surface-active agent (sodium laureth sulfate): proper amount

[0038] Next, a segment having a size of 2-cm square was cut from the center portion of the specimen (electroformed body). The segment was halved so that each half had a width of 1 cm. One half was used as Sample (1) for measuring the hardness and crystal-grain diameter. The other half was used as Sample (2) for ion implantation.

[0039] The hardness was measured by the following method. Sample (1) was embedded into epoxy resin vertically so that the cross section could be level with the surface of the resin. The cross section was polished with abrasive by varying the particle size of the abrasive grain to the grain-size number of 4,000 successively. Then, the cross section was treated by buffing to obtain a mirror-finished surface. The hardness was measured at a position 25 μm away from the plated surface of the sample with a Vickers hardness tester. Ten measurements were conducted to obtain the average value. The crystal-grain diameter was measured with X-ray diffraction.

[0040] Sample (2) (electroformed body) was subjected to an omnidirectional ion implantation under the following conditions:

[0041] {Conditions of Omnidirectional Ion Implantation}

[0042] Voltage: 30 kV

[0043] Type of implanted ion: carbon (C)

[0044] Pulse frequency: 150 kHz

[0045] Treated time: 60 minutes

[0046] Ultimate vacuum degree: 6.7×10^{-4} Pa or below

[0047] Temperature: substrate holder was cooled with a coolant at 25° C.

[0048] After the ion implantation, the Vickers hardness and crystal-grain diameter were measured as with Sample (1).

[0049] (Results of the Measurements)

[0050] Sample (1) had a Vickers hardness, Hv, of 439 and crystal-grain diameters of 10 to 1,000 nm. Observation by scanning ion microscopy (SIM) after an FIB treatment confirmed that there were minute voids on the order of nanometers.

[0051] On the other hand, the ion-implanted electroformed structural material showed an increased Vickers hardness, Hv, of 511 at a position deeper than the ion-implanted layer. The crystal-grain diameter decreased to the range of 5 to 250 nm at the same position. The observation by SIM after an FIB treatment revealed that the voids observed in Sample (1) became smaller and their density decreased significantly.

[0052] The findings obtained from other embodiments of the present invention as well as the above-described embodiment are explained below on an enumerative basis.

[0053] (1) In the above-described ion-implanted electroformed structural material, an ion-implanted layer can be formed in the surface portion ranging from the surface to a depth of at most 5 μm, and a structure in which the microstructure is modulated can be produced at a position deeper than the ion-implanted layer.

[0054] The above-described structure in which the microstructure of an electroformed body is modulated means a structure into which the microstructure as electroformed is transformed such that crystal grains finer than the crystal grains as electroformed make up the principal portion. This structure enables the production of a minute structural material having excellent durability. If ion implantation is intended to reach a depth of more than 5 μm from the surface, an exceedingly large-scale accelerator is required. This system deviates from the object of the present invention, which is to increase the strength easily.

[0055] The modulation of the microstructure may be produced at a cross-sectional center position, deep in the interior from the surface of the electroformed structural material.

[0056] As described above, why the above-described modulated structure is produced by ion implantation, how deep the modulated structure is formed from the surface, and so on are yet to be clarified. Nevertheless, the modulated structure is formed throughout the thickness of an electroformed structural material having a thickness of 80 μm or so. Once the modulated structure is produced, it may be produced in the entire cross section. In other words, the depthwise distribution of the modulated structure may not be controlled. However, when the modulated structure having a finer structure is formed at least at the cross-sectional center position, this structure is highly useful for the improvement of the durability of the electroformed structural material.

[0057] (2) According to the present invention, the portion at which the above-described modulation of the microstructure is produced can have an average crystal-grain diameter of at most 0.5 μm. The formation of the modulated structure having a finer structure can improve the strength. As shown in FIGS. **5** to **8**, when the structure of the electroformed body having a columnar crystal structure is modulated, the columnar crystal preserves the shape of the columnar crystal while it becomes finer. In the columnar crystals, the average crystal-grain diameter is an average grain diameter in a section parallel to the growth direction of the columnar crystals.

[0058] As described above, according to the present invention, the modulation of the microstructure and the decrease in average crystal-grain diameter at a position deeper than the ion-implanted layer can cause the portion at which the microstructure is modulated to have a hardness higher than that of the electroformed body at the time it is formed by electroforming.

[0059] (3) The electroformed body formed by electroforming is a material into which ions are to be implanted. When the electroformed body itself has a fine structure, it is easy to produce the modulated structure at an interior portion by the ion implantation. The modulated structure produced by the ion implantation has a finer structure and a higher strength than those of the electroformed body.

[0060] It is desirable that the electroformed body formed by electroforming have an average crystal-grain diameter of at most 1 μm. In the case of the columnar crystals, the average grain diameter is the average value of the grain diameters at the longitudinal section of the columnar crystals. The above requirement can be achieved by applying a pulse-shaped voltage at the time of the electroforming. The application of the pulse-shaped voltage, or the supply of the pulse-shaped current, can increase the degree of the supersaturation at the time of the deposition from the solution. This increase can increase the density of the nucleus evolution, causing the electroformed body to have a finer structure. This operation facilitates the formation of the modulated structure having a finer structure at a position deeper than the ion-implanted layer when ions are implanted.

[0061] (4) In the step of the implanting of ions, the ion implantation into a region ranging from the surface to a depth of at most 5 μm can increase the hardness of a portion deeper than the region. In other words, because the modulated structure having a finer structure can be formed at a position deeper than the ion-implanted layer, the interior portion beyond the reach of the ions can have an increased strength.

[0062] In the above-described step of the implanting of ions, the ion implantation into a region ranging from the surface to a depth of at most 5 μm can modulate the structure of a portion deeper than the region. According to this method, even when the ion-implanted layer is formed in a region ranging from the surface to a depth of at most 5 μm, the portion at a depth of, for example, 40 μm from the surface can have a modulated structure having a finer structure.

[0063] (5) In the step of the implanting of ions, the temperature of the electroformed body may be maintained at most one-third the melting point (expressed in K) of the material that forms the electroformed body. This condition maintains the decreased diameter of the individual crystal grains in the modulated structure having a finer structure, so that the fine grains can be prevented from growing to get coarse.

[0064] (6) In the step of the implanting of ions, it is desirable that the ions be accelerated at a voltage of at least 10 kV. If the accelerating voltage is less than 10 kV, the ions cannot be implanted sufficiently, so that it is difficult, if not impossible, to form the modulated structure having a finer structure at the interior.

[0065] (7) In the step of the implanting of ions, it is desirable to use an omnidirectional plasma ion-implanting unit. This unit can form the ion-implanted layer uniformly at the entire surface without producing shaded portions even for an electroformed body having a complicated shape. As a result, the modulated structure having a finer structure can be formed thoroughly at a position deeper than the ion-implanted layer.

[0066] (8) It is desirable that the electroformed body be made of a material selected from the group consisting of Ni, Fe, copper (Cu), zinc (Zn), tin (Sn), Mn, Co, silver (Ag), gold (Au), and alloys of these. An ion-implantation treatment of the electroformed body made of the foregoing material can produce an ion-implanted electroformed structural material having excellent durability.

[0067] (9) In the above embodiment, a carbon (C) ion was used as the ion to be implanted into the electroformed body. Nevertheless, other ions may be used. For example, a nitrogen (N) ion may be used. The ion may be either an atomic ion or a molecular ion. Of course, other ions than the carbon and nitrogen ions may be used.

[0068] Embodiments of the present invention are explained above. The above-described embodiments of the present invention are strictly for the purpose of exemplification. The scope of the present invention is not limited by the above-described embodiments of the present invention. The scope of the pre-sent invention is shown by the description of the scope of the appended claims. Furthermore, the present invention is intended to cover all modifications included within the meaning and scope equivalent to the scope of the claims.

1-6. (canceled)

7. A method of producing an ion-implanted electroformed structural material, the method comprising the steps of:

(a) forming an electroformed body; and

(b) implanting accelerated ions into the electroformed body.

8. A method of producing an ion-implanted electroformed structural material as defined by claim **7**, wherein in the step of forming an electroformed body, the electroformed body is formed such that it has an average crystal-grain diameter of at most 1 μm.

9. A method of producing an ion-implanted electroformed structural material as defined by claim **7**, wherein in the step of forming an electroformed body, a pulse-shaped voltage is applied.

10. A method of producing an ion-implanted electroformed structural material as defined by claim **7**, wherein in the step of implanting ions into the electroformed body, the ions are implanted in a region ranging from the surface to a depth of at most 5 μm to increase the hardness of a portion deeper than the region.

11. A method of producing an ion-implanted electroformed structural material as defined by claim **7**, wherein in the step of implanting ions into the electroformed body, the ions are implanted in a region ranging from the surface to a depth of at most 5 μm to modulate the structure of a portion deeper than the region.

12. A method of producing an ion-implanted electroformed structural material as defined by claim **7**, wherein in the step of implanting ions into the electroformed body, the temperature of the electroformed body is maintained at most one-third the melting point (expressed in K) of the material that forms the electroformed body.

13. A method of producing an ion-implanted electroformed structural material as defined by claim **7**, wherein in the step of implanting ions into the electroformed body, the ions are accelerated at a voltage of at least 10 kV.

14. A method of producing an ion-implanted electroformed structural material as defined by claim **7**, wherein in the step of implanting ions into the electroformed body, an omnidirectional plasma ion-implanting unit is used.

* * * * *