(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 2 752 502 A1

(12) EUROPEAN PATENT APPLICATION

published in accordance with Art. 153(4) EPC

(43) Date of publication:
09.07.2014 Bulletin 2014/28

(21) Application number: **12828406.4**

(22) Date of filing: **03.08.2012**

(51) Int Cl.:
C23C 18/36 *(2006.01)*

(86) International application number:
PCT/JP2012/069872

(87) International publication number:
WO 2013/031483 (07.03.2013 Gazette 2013/10)

(84) Designated Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR

(30) Priority: **31.08.2011 JP 2011190136**

(71) Applicant: **Kabushiki Kaisha Toyota Chuo Kenkyusho**
Nagakute-shi, Aichi 480-1192 (JP)

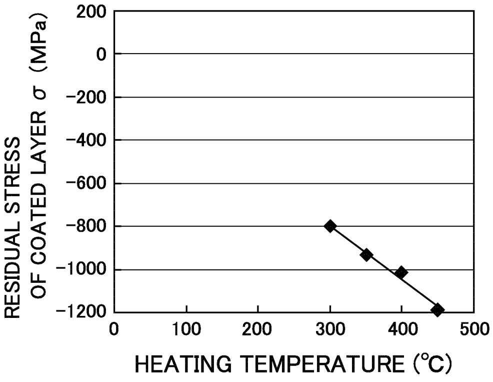
(72) Inventors:
- **YAMADA Yuka**
  Nagakute-shi
  Aichi 480-1192 (JP)
- **MATSUOKA Hideaki**
  Nagakute-shi
  Aichi 480-1192 (JP)
- **SUZUKI Ken-ichi**
  Nagakute-shi
  Aichi 480-1192 (JP)
- **KITAHARA Gaku**
  Nagakute-shi
  Aichi 480-1192 (JP)

(74) Representative: **Kramer - Barske - Schmidtchen**
Landsberger Strasse 300
80687 München (DE)

(54) ABRASION-RESISTANT MEMBER MADE FROM ALUMINUM ALLOY, AND METHOD FOR PRODUCING SAME

(57) Provided is a wear resistant aluminum alloy member. The wear resistant aluminum alloy member of the present invention comprises a substrate comprising an aluminum alloy, and a coated layer coating at least part of a surface of the substrate, and is characterized in that the aluminum alloy has a residual hardness of 120 Hv or more when measured in a room temperature state after held in an atmospheric pressure environment at 400 deg. C for 10 hours; and the coated layer comprises a crystalline Ni-P layer comprising Ni and Ni_3P. This crystalline Ni-P layer can be obtained by heating a Ni-P plated layer, which has been formed on the surface of the substrate by electroless Ni-P plating, for example, at 300 deg. C or more. Compressive residual stress is imparted to the crystalline Ni-P layer. It is preferred that the aluminum alloy contains 1 to 7 % of Fe because a crystalline Ni-P layer having high adhesion can be obtained.

FIG.3



EP 2 752 502 A1

Printed by Jouve, 75001 PARIS (FR)

Description

Technical Field

[0001] The present invention relates to a wear resistant aluminum alloy member and a method for producing the same.

Background Art

[0002] With the recent increase in environmental awareness, fuel consumption reduction and weight reduction, which is effective in reducing CO_2 emissions, etc. have been strongly promoted in a field of transportation equipment such as automobiles, motorcycles and aircraft. Therefore, component members which have been conventionally constituted by steel members and cast iron members are being replaced with aluminum alloy members.

[0003] In promoting the replacement to the aluminum alloy members, an emphasis has recently been placed not only on their heat resistance but also on their wear resistance, corrosion resistance, fatigue strength and so on. Under these circumstances, descriptions on wear resistant aluminum alloy members having hard layers on their surfaces are found in the following patent literature.

Citation List

Patent Literature

[0004]

[PTL 1] Japanese Patent No. 3009527
[PTL 2] Japanese Unexamined Patent Publication No. 2004-277784

Summary of Invention

Problems to be Solved by Invention

[0005] Processes for forming a hard layer or the like on an aluminum alloy are classified into dry processes and wet processes. The dry processes are processes for forming a hard layer of TiN, CrN, DLC, Al_2O_3 or the like on a surface of a substrate by PVD, CVD, ion nitriding, thermal spraying, etc. The wet processes are processes for forming an anodic oxide layer or other various plated layers on a surface of an aluminum alloy by immersing the aluminum alloy in a certain solution.

[0006] Films formed by the dry processes have a Vickers Hardness of about 1000 to 3000 Hv and are harder than those formed by the wet processes. However, the dry processes are low in mass productivity and high in equipment costs and processing costs.

[0007] On the other hand, the wet processes facilitate productivity improvement, cost reduction, and so on. However, of hard layers formed by the wet processes, Cr plated layers, which have good wear resistance, (800 to 1000 Hv) are not environmentally preferable because of use of hexavalent chromium. In a case of composite plating (dispersion plating), plating solutions are difficult to be controlled because of their instability.

[0008] In contrast to these plating processes, electroless Ni-P plating poses relatively little environmental problem and has good mass productivity. However, Ni-P plated layers are not as hard as films formed by dry processes or Cr plated layers, and generally lack wear resistance. Even a relatively hard low-P concentration Ni-P plated layer has a Vickers hardness of 500 to 700 Hv. It is known that upon heated to 300 deg. C or more, the Ni-P plated layers can attain a maximum hardness of 900 to 1000 Hv, which is comparable to Cr plated layers. Such heating, however, softens an aluminum alloy as a substrate (a base material) and prevents a resulting member from obtaining necessary strength. Moreover, when a large load is applied on the member, the Ni-P plated layer sometimes cannot follow deformation of the substrate and may crack or peel off. As described heretofore, it is conventionally difficult for an aluminum alloy member to secure wear resistance by a Ni-P plated layer.

[0009] The present invention has been made in view of these circumstances. It is an object of the present invention to provide an aluminum alloy member having improved wear resistance by Ni-P plating, while taking mass productivity, production costs, and environmental friendliness into consideration. It is also an object of the present invention to provide a method for producing the same.

Solutions to Problems

[0010] The present inventors have made earnest researches in order to solve these problems and succeeded in hardening a Ni-P plated layer formed on a surface of a substrate comprising an aluminum alloy without softening the aluminum alloy substrate. The present inventors have made further researches on the basis of this fruit and completed the following present invention.

[Wear Resistant Aluminum Alloy Member]

[0011]

(1) A wear resistant aluminum alloy member of the present invention comprises a substrate comprising an aluminum alloy, and a coated layer coating at least part of a surface of the substrate, and is characterized in that the aluminum alloy has a residual hardness of 120 Hv or more when measured in a room temperature state after held in an atmospheric pressure environment at 400 deg. C for 10 hours, and the coated layer comprises a crystalline Ni-P layer comprising nickel (Ni) and phosphorus (P) and being crystalline.

(2) The wear resistant aluminum alloy member of the present invention (hereinafter referred to as the "wear resistant member" when appropriate) exhibits good wear resistance because a surface of its substrate is coated with a coated layer comprising a crystalline Ni-P layer. Moreover, the wear resistant member of the present invention can also exhibit good heat resistance, corrosion resistance, fatigue resistance and durability. However, reason why the wear resistant member of the present invention exhibits good characteristics is not all clear. The reason is assumed as follows under the present circumstances.

[0012] First of all, the crystalline Ni-P layer is very hard, unlike an amorphous Ni-P plated layer formed by electroless Ni-P plating or the like (hereinafter referred to as the "amorphous Ni-P layer" when appropriate). This crystalline Ni-P layer, not only when having a low P concentration but also when having a high P concentration, exhibits a sufficient hardness in accordance with degree of crystallinity. This is supposed to be because the crystalline Ni-P layer has a composite structure in which a precipitate phase such as Ni_3P is dispersed in a crystallized Ni parent phase.

[0013] Second, a high compressive residual stress may occur in the crystalline Ni-P layer. This compressive residual stress is assumed to be caused by a difference in thermal expansion volume between the coated layer and the substrate, and precipitation of crystalline Ni and Ni-P upon heating of the amorphous Ni-P layer. Specifically speaking, when a member comprising a substrate and a coated layer is heated, the coated layer thermally expands without peeled off from the thermally expanding substrate just like the substrate expands. While temperature of the member is increased or kept high after the temperature rise, a crystalline Ni phase and a crystalline Ni-P phase precipitate from the amorphous Ni-P layer, but the coated layer mainly comprised of the crystalline Ni phase and the crystalline Ni-P phase has a different thermal expansion coefficient from that of the substrate. Therefore, while temperature of the member decreases, the coated layer and the substrate have a difference in thermal shrinkage volume. As a result, it is supposed that compressive residual stress is generated in the crystalline Ni-P layer having a smaller thermal expansion coefficient than that of the substrate.

[0014] The crystalline Ni-P layer in which such compressive residual stress is present hardly cracks. This contributes not only to an improvement in wear resistance but also to an improvement in corrosion resistance and fatigue strength under repeated application of load (an improvement in fatigue resistance) or the like.

[0015] By the way, even if the amorphous Ni-P layer is crystallized or the crystalline Ni-P layer is heated at elevated temperatures so as to generate compressive residual stress, the substrate exhibits a sufficient residual hardness and retention of the crystalline Ni-P layer and functions of the wear resistant member can be secured. Therefore, it is supposed that the wear resistant member of the present invention stably exhibits good wear resistance owing to a synergistic action of the substrate having good softening resistance and the crystalline Ni-P layer (the coated layer) having good wear resistance.

[0016] Note that because comprising the substrate and the coated layer having good high temperature characteristics, the wear resistant member of the present invention can exhibit sufficient wear resistance and strength and so on even in a high temperature environment.

[Method for Producing Wear Resistant Aluminum Alloy Member]

[0017]

(1) The present invention can be grasped not only as the abovementioned wear resistant member but also as a method for producing the same. That is to say, the present invention can be grasped as a method for producing the

abovementioned wear resistant aluminum alloy member, which is characterized by having a plating step of forming a Ni-P plated layer on a surface of a substrate by bringing the surface of the substrate in contact with an electroless Ni-P plating solution; and a crystallizing step of crystallizing the Ni-P plated layer by heating the Ni-P plated layer.
(2) According to the production method of the present invention, the aforementioned crystalline Ni-P layer can be easily formed by heating an amorphous Ni-P plated layer, which has been formed on a surface of a substrate by electroless Ni-P plating, at a predetermined temperature. Therefore, this production method can mass-produce the aforementioned wear resistant member efficiently at low costs without causing significant environmental problems.

[Others]

[0018]

(1) The "residual hardness" mentioned herein means a hardness of an object subjected to a predetermined heat treatment step measured in a room temperature state by a Vickers hardness tester. More specifically, the residual hardness is an average of hardness values of a cross section of the object measured five times under a test load of 0.245 N, and a load dwell time of 20 seconds using a micro Vickers hardness tester.

[0019] Preferably, the aluminum alloy of the present invention has a residual hardness of not less than 120 Hv, not less than 130 Hv, not less than 140 Hv, or not less than 145 Hv after held in an atmospheric pressure environment at 400 deg. C for 10 hours. It should be noted that in measuring the residual hardness, basically heat history (history of usage) of the aluminum alloy is not limited. It is only necessary that an aluminum alloy attached firmly by a crystalline Ni-P layer has a residual hardness of 120 Hv or more when measured after subjected to the above heat treatment.

(2) The "residual stress" mentioned herein is determined by the Standard Method for X-Ray Stress Measurement (The Committee on X-ray Study of Mechanical Behavior of Materials in the Society of Materials Science, Japan (1997)). More specifically, the residual stress is determined by radiating Cu-Kα characteristic X-rays on a surface of a sample and applying the $\sin^2\psi$ method to an obtained diffraction peak of Ni (311) . A necessary stress constant in determining residual stress was determined from Young's modulus and Poisson's ratio of nickel.

[0020] As mentioned before, compressive residual stress is present in the crystalline Ni-P layer. A value of compressive residual stress is not limited, but it is preferred that the value of compressive residual stress is not less than 200 MPa, not less than 300 MPa, or not less than 900 MPa. It should be noted that residual stress present in the crystalline Ni-P layer can be greater in proportion with an increase in heating temperature.

(3) The aluminum alloy of the present invention is not limited in form, metallic structure or processing stage. For example, the aluminum alloy of the present invention can be an ingot, rapidly solidified powder, a ribbon or its milled powder, a molding or a billet, a sintered material, a wrought material (an extruded material, etc.), or can be a raw material, an intermediate product, or a final product.
(4) A range "x to y" mentioned herein includes a lower limit value x and an upper limit value y, unless otherwise specified. A new numerical range "a to b" can be set by using various numerical values mentioned herein or any numerical values contained in various numerical ranges as a new lower limit value or a new upper limit value.

Brief Description of Drawings

[0021]

[Fig. 1] Fig. 1 is a graph showing a relation between heating temperature and hardness of substrates.
[Fig. 2] Fig. 2 is a graph showing a relation between heating temperature and hardness of coated layers.
[Fig. 3] Fig. 3 is a graph showing a relation between heating temperature and residual stress of coated layers.
[Fig. 4] Fig. 4 shows X-ray diffraction images of respective coated layers.
[Fig. 5A] Fig. 5A is a photograph showing an appearance of an aluminum alloy of Base Material No. 11 with electroless Ni-P plating.
[Fig. 5B] Fig. 5B is a photograph showing an appearance of an aluminum alloy of Base Material No. C3 with electroless Ni-P plating.
[Fig. 6A] Fig. 6A is a view showing a cross-sectional shape of a wear track of Specimen No. 1 after a ball-on-disk test.
[Fig. 6B] Fig. 6B is a view showing a cross-sectional shape of a wear track of Specimen No. 2 after the ball-on-disk test.
[Fig. 6C] Fig. 6C is a view showing a cross-sectional shape of a wear track of Specimen No. 3 after the ball-on-disk test.

Modes for Carrying Out the Invention

[0022] A subject matter described herein can be applied not only to the wear resistant member of the present invention but also to the method for producing the same. A constituent element of the production method can be a constituent element of the object when understood as a product by process. Any one or more constituent elements selected from the present description can be added to the aforementioned constituent elements of the present invention. Which embodiment is best or not differs depending on application targets, required performance and so on.

[Coated Layer]

[0023] The coated layer of the present invention comprises a crystalline Ni-P layer, but the term "crystalline" does not mean that the entire coated layer needs to be a perfect crystal. It is sufficient that crystalline portions are present to a degree to be detected by X-rays. Moreover, element composition or metallic structure of the crystalline Ni-P layer is not limited in the present invention. The metallic structure of the crystalline Ni-P layer is not specified in general, but is supposed to be constituted, for example, by a crystalline phase of Ni and a precipitate phase of Ni_3P or the like. This metallic structure differs depending on element composition, degree of crystallization, heat history, etc. of the crystalline Ni-P layer.

[0024] A P content in the crystalline Ni-P layer is appropriately controlled with a use purpose, function, required specification and so on of the wear resistant member. However, if the crystalline Ni-P layer (especially when formed through electroless Ni-P plating) contains 1 to 13 % by mass of P when a total mass of the layer is taken as 100 % by mass (hereinafter simply referred to as "%"), a uniform plated layer is stably formed. That is to say, if the P content is excessively small, a content of sodium hypophosphite or the like as a reducing agent is small, so reducing power decreases and plating is hard to precipitate. If the P content is excessively large, a plating solution is unstable and realistically it is difficult to plate a substrate. However, unlike an amorphous Ni-P plated layer, the crystalline Ni-P layer of the present invention can exhibit a sufficient hardness even when containing a large amount of P.

> (2) The crystalline Ni-P layer of the present invention is obtained, for example, by heating a Ni-P plated layer, which has been formed on a surface of a substrate by electroless Ni-P plating, at 300 to 500 deg. C, more preferably, 350 to 450 deg. C. The Ni-P plated layer as formed by electroless Ni-P plating is amorphous and may keep the amorphous phase until about 200 deg. C. However, if the amorphous Ni-P plated layer is heated to 200 deg. C or more, crystallization gradually proceeds. In accordance with degree of crystallization, hardness of the crystalline Ni-P layer and compressive residual stress present in the crystalline Ni-P layer can also increase.

[0025] Of course, the crystalline Ni-P layer can be obtained not only by electroless Ni-P plating but also by electrolytic Ni-P plating. While electroless Ni-P plating causes P to be co-deposited using sodium hypophosphite as a reducing agent, electrolytic Ni-P plating causes P to be co-deposited by using sodium phosphite. In electrolytic Ni-P plating, electric current density easily changes with shape of a substrate, and the amount of P to be co-deposited and plated layer thickness are not easy to be controlled. Therefore, it is preferred that the crystalline Ni-P layer of the present invention is formed via electroless Ni-P plating.

[Coated Layer Formation (Method for Producing Wear Resistant Member)]

[0026] The coated layer of the present invention is not limited in its forming method, and is formed, for example, by the following electroless Ni-P plating method.

(1) Cleaning Step

[0027] A cleaning step removes an oxide layer formed on a surface of a substrate, oil stains attached on the surface of the substrate by machine processing, and so on. Owing to this cleaning step, a next pretreatment step can be efficiently performed and adhesion of a Ni-P plated layer, etc. can be improved.

[0028] For example, the cleaning step comprises an etching step of removing an oxide layer by bringing the substrate in contact with an alkaline solution, and a desmutting step of removing smut formed after the etching step with an acid solution. Kind and concentration of the alkaline solution and the acid solution can be suitably controlled. If the cleaning step is performed by chemical polishing or electrolytic polishing instead of these steps, smoothing of the substrate surface can also be achieved.

(2) Pretreatment Step (Zincate Treatment Step, Activating Step)

[0029] An aluminum alloy is a difficult material to be plated. Even if a cleaning step is performed, as soon as contacting the air, an aluminum alloy is covered with a dense strong oxide layer and becomes inactive and formation of a Ni-P plated layer is liable to be blocked.

[0030] Therefore, when an aluminum alloy is to be plated, zincate treatment is often applied as a pretreatment step. The zincate treatment is a treatment to bring a substrate in contact with a zincate solution (for example, an aqueous sodium hydroxide solution in which zinc oxide is dissolved), thereby forming zinc substitution plating to serve as an intermediate coated layer on a surface of the substrate. This zincate treatment facilitates formation of a Ni-P plated layer having high adhesion on the substrate surface. Particularly when zincate treatment is performed twice or more, a Ni-P plated layer having high adhesion can be easily obtained. Therefore, zincate treatment is also effective in the present invention as one pretreatment of plating.

[0031] However, if electroless Ni-P plating is performed after the zincate treatment, most of the zinc constituting the intermediate coated layer dissolves into a plating solution. Therefore, the plating solution is contaminated and life of the expensive plating solution is shortened. This is uneconomical.

[0032] Therefore, it is suitable to perform an activating step which allows direct plating on the substrate surface without performing the zincate treatment. This activating step is a step of activating the substrate surface by bringing the substrate surface in contact with a treatment solution of pH 3 to 12. This treatment solution (the activating treatment solution) is classified into an acid activating treatment solution and an alkaline activating treatment solution. Examples of the acid activating treatment solution include hydrochloric acid, hydrofluoric acid, and an aqueous solution of ammonium hydrogen fluoride. Examples of the alkaline treatment solution include aqueous solutions of sodium hydroxide, sodium carbonate, ammonium hydroxide, or various amines. Of course, it is preferred that the activating step is performed after the cleaning step. However, when an acid activating treatment solution is employed, the activating step can also serve as the aforementioned cleaning step.

[0033] Note that the activating step has the following meaning. When electroless plating is performed on an aluminum-based substrate, since aluminum as an element does not have catalytic activity for starting a reaction of a reducing agent, electroless plating reaction does not automatically start. However, practical aluminum-based substrates contain more than a subtle amount of elements having catalytic activity such as iron and nickel as impurities or adding elements. If these elements can be exposed to a surface of an aluminum-based substrate, the electroless plating reaction can automatically start. However, a surface of the aluminum-based substrate which has been through a cleaning step such as degreasing, etching, and immersion in acid is covered with a passive layer (aluminum oxide) and the aforementioned active sites comprising precipitates of iron, nickel, etc. are not sufficiently exposed. Even if the aluminum-based substrate in this stage is immersed in an electroless plating solution, a plating reaction does not start. Therefore, as the passive layer is removed by the activating treatment after the cleaning step, exposure of active sites proceeds. Then, if immersion potential shifts to -1.4 to -1.35 V (vs Ag/AgCl), exposure of the active sites (activation) becomes sufficient and electroless plating automatically starts on the aluminum-based substrate.

[0034] The activating step for about several minutes is sufficient but can be applied twice or more, if necessary. In any case, it is important that the substrate surface is sufficiently activated by this activating step. This judgment can be done by whether natural (standard) electrode potential of the substrate subjected to activating treatment is high or low. The natural electrode potential can be measured, for example, by immersing the substrate after the activating treatment and an Ag/AgCl electrode in an alkaline aqueous solution controlled to pH 11.5 (a measurement solution) and immediately measuring natural electrode potential of the substrate by a potentiometer. When this natural electrode potential shifts to -1.4 to -1.35 V, it is determined that the substrate surface is suitably activated for plating. That is to say, the activating step of bringing the substrate surface in contact with the activating treatment solution should be made until natural electrode potential of the substrate reaches a desired value.

[0035] It should be noted that, if activating conditions which are necessary for the natural electrode potential to obtain a desired value can be determined, the natural electrode potential does not have to be measured every time, and the activating step only needs to be carried out under these conditions. Note that when the natural electrode potential is measured, a measurement solution can also serve as an activating treatment solution. Details of the activating step other than those mentioned above are found in Japanese Patent No. 2648716.

(3)Plating Step

[0036] The plating step forms a Ni-P plated layer on the pretreated substrate surface. This Ni-P plated layer is efficiently formed by using an electroless Ni-P plating solution. Composition and temperature of the electroless plating solution, and plating time can be suitably controlled.

[0037] The Ni-P plated layer immediately after plating is amorphous and does not always have high adhesion. In order to improve the adhesion, the substrate after the plating step can be heated at about 200 deg. C for about one hour independently of a next crystallizing step.

(4) Crystallizing Step

[0038] The crystallizing step changes the amorphous Ni-P plated layer formed on the substrate surface into a hard crystalline Ni-P plated layer. In this crystallizing step, it is basically suitable to heat the Ni-P plated layer at 300 to 500 deg. C or preferably 350 to 450 deg. C. Heating time of this heating can be about 0.5 to 10 hours.

[Substrate]

[0039] The substrate comprises an aluminum alloy which does not soften even if heated in the crystallization step. The aluminum alloy only needs to have such a softening resistance to have a residual hardness of 120 Hv or more when measured in a room temperature state after held at 400 deg. C for 10 hours, and its composition or producing method is not limited. For example, the following aluminum alloy is suitably employed.

<Aluminum Alloy Composition>

(1) Fe

[0040] Fe is an element which enhances strength, hardness and the like of an aluminum alloy. Specifically, a proper amount of Fe forms an intermetallic compound with Al (an Al-Fe based intermetallic compound: a first compound phase) in a parent phase (a-Al phase). This first compound phase enhances strength and hardness of the aluminum alloy.

[0041] It is preferred that the aluminum alloy contains 1 to 7 %, 3 to 6 %, 4 to 6 %, or 4.5 to 5.5 % of Fe when a total mass of the aluminum alloy is taken as 100 % by mass (hereinafter this phrase is omitted) . If the Fe content is excessively small, the aluminum alloy cannot obtain a sufficient strength or hardness. If the Fe content is excessively large, ductility decreases and strength is too high, so the aluminum alloy is difficult to be shaped or processed.

[0042] It should be noted that Fe is not only effective in increasing strength of the aluminum alloy but also capable to serve as a catalytic element (an activating element) in the aforementioned electroless Ni-P plating. That is to say, if Fe is partially exposed to the substrate surface after the aforementioned activating treatment step, exposed points act as starting points of formation of a Ni-P plated layer. Therefore, a Ni-P plated layer having high adhesion and uniformity is formed by using a Fe-containing aluminum alloy as a substrate. This tendency is greater as the Fe content of the aluminum alloy increases in a range of 1 % or more.

(2) Zr and Ti

[0043] Zr and Ti are important elements in forming a second compound phase, which improves heat resistance of the aluminum alloy, in cooperation with Al. The aforementioned first compound phase is not always thermally stable and may undergo phase transformation or shape change (coarsening) when exposed to a high temperature atmosphere for a long time.

[0044] Proper amounts of Zr and Ti form an Al-(Zr, Ti) based intermetallic compound having $L1_2$ structure (a second compound phase or a precipitate phase) together with Al. This second compound phase is coherent with the parent phase, and appears in neighborhood of a boundary (an interface) between the Al-Fe based intermetallic compound and the parent phase and is stable up to a high temperature range. Specifically speaking, the second compound phase hardly undergoes phase transformation or coarsening at least at or below a temperature at which the phase starts precipitating. Moreover, the second compound phase which has precipitated in the neighborhood of a boundary between the first compound phase and the parent phase stably suppresses (what is called, pins) the first compound phase, which contributes to strength and hardness of the aluminum alloy, from undergoing phase transformation, shape change or the like at elevated temperatures. It is supposed that an aluminum alloy exhibiting good softening resistance and heat resistance can be obtained owing to a synergistic action of the first compound phase and the second compound phase.

[0045] It should be noted that the term "coherent" herein means that the second compound phase has the same basic crystal structure as the parent phase and atomic planes or atomic rows are continuous without excess or shortage at a boundary (an interface) between the second compound phase and the parent phase. Although dislocation induced by processing may cause irregularities of atomic rows or point defects, these are not taken into consideration.

[0046] By the way, it is known that the second compound phase has a nanoparticle shape and has a high Zr concentration at its center and a high Ti concentration at its outer periphery. That is to say, it is known that Zr and Ti concentrations in Al_3 (Zr, Ti) are inclined from the center to the outer periphery. In order to form such a second compound phase, it is suitable that Zr is present in a larger amount than Ti and that a ratio by mass of Zr to Ti (Zr/Ti) falls in a predetermined range.

[0047] Therefore, it is preferred that Zr is contained in a range of 0.5 to 3%, 0.66 to 1.5 %, 0.7 to 1.3 %, or 0.8 to 1.2

%. Furthermore, it is preferred that Ti is contained in a range of 0.5 to 3 %, 0.6 to 1 %, or 0.7 to 0.9 %. If the Zr content or the Ti content is excessively small, the effect decreases. If the Zr content or the Ti content is excessively large, melting temperature is extremely high, so production costs are high and Zr and Ti tend to form coarse crystalized or precipitated products together with Al, and workability and formability of the aluminum alloy tend to be low.

[0048] Moreover, when a ratio by mass of the two elements (Zr/Ti) is in a range of 1.1 to 1.5 or 1.15 to 1.4, an aluminum alloy which is stable up to a high temperature range can be easily obtained owing to formation of the second compound phase.

[0049] It should be noted that in order to finely disperse the second compound phase in the parent phase in neighborhood of a boundary with the first compound phase, it is only necessary to form a solid solution of sufficient amounts of Zr and Ti in a base metal (a supersaturated solid solution of Zr and Ti) and later precipitate Zr and Ti. Specifically speaking, it is only necessary to form a supersaturated solid solution of appropriate amounts of Zr and Ti by rapid solidification and then apply energy as driving force to promote precipitation of Zr and Ti. Examples of such energy include heat energy applied by heat treatment, hot working, etc., and strain energy applied by plastic working, etc. Heat energy can be singly applied by heat treatment or heat energy and strain energy can be simultaneously applied by hot working, etc. Furthermore, heat energy can be applied after strain energy is applied, for example, by applying heat treatment after cold working or hot working. If both heat energy and strain energy are applied, precipitation of the second compound phase is accelerated, so a heat-resistant high-strength aluminum alloy can be efficiently obtained in a short time.

(3) Mg

[0050] Mg is an effective element in improving strength (especially strength at room temperature) of an aluminum alloy. It is preferred that a Mg content is in a range of 0.5 to 5 %, 0.6 to 2.2 %, 1 to 2 %, or 1.2 to 1.8 %. An excessively small Mg content exhibits no effect, while an excessively large content causes a decrease in workability and formability of the aluminum alloy.

> (4) In consideration of the forgoing discussion, it is preferred that the aluminum alloy of the present invention has an alloy composition comprising: 3 to 6 % of Fe, 0.66 to 1.5 % of Zr, 0.6 to 1 % of Ti, a ratio by mass of Zr to Ti (Zr/Ti): 1.1 to 1.5, and a remainder being Al and inevitable impurities with/without (a) reforming element(s).

[0051] The "reforming element" mentioned herein is an element which is other than Al, Fe, Zr, Ti and Mg and is effective in improving a characteristic of the aluminum alloy. The characteristic to be improved is not limited in kind and is exemplified by strength, hardness, toughness, ductility, and dimensional stability in a high temperature range or a room temperature range. Specific examples of such a reforming element includes Cr, Co, manganese (Mn), nickel (Ni), scandium (Sc), yttrium (Y), lanthanum (La), vanadium (V), hafnium (Hf), and niobium (Nb). Mixing ratio of respective elements is arbitrarily chosen but in general their contents are extremely small.

[0052] The "inevitable impurities" are impurities contained in raw materials to be melted or impurities mixed during the respective steps, and are elements which are difficult to be removed for cost or technical reasons. An example of inevitable impurities in the aluminum alloy of the present invention is silicon (Si).

<Metallic Structure of Aluminum Alloy>

[0053] The aforementioned aluminum alloy has a composite structure having at least the Al parent phase (α phase), the Al-Fe based intermetallic compound phase (the first compound phase), and the Al-(Zr, Ti) based intermetallic compound (the second compound phase).

[0054] It is preferred that the second intermetallic compound phase has an average size in a range of 1 to 30 nm, 2 to 20 nm, or 3 to 15 nm. When this size is excessively small or excessively large, the effect of the second compound phase to improve heat resistance of the aluminum alloy may decrease. Please note that the average size is a value obtained by observing a sample selected at random from the aluminum alloy through a transmission electron microscope (TEM) and analyzing an average diameter of more than 30 dispersed nanoparticles of the second compound phase by image processing technique.

<Method for Producing Aluminum Alloy>

[0055]

> (1) The abovementioned aluminum alloy can be produced by a variety of methods. For example, it is possible to employ a method for producing the aluminum alloy which comprises a solidifying step of obtaining a solid body by

rapidly solidifying a molten alloy at a cooling rate of 100 deg. C/sec. or more, and a heat treatment step of heating the solid body, for example, at 300 to 500 deg. C. It is suitable that this heat treatment step is a hot working step of applying hot plastic working to the solid body, because it allows to obtain a metallic structure in which the aforementioned second compound phase is ultrafinely and uniformly dispersed in a base metal.

[0056] The rapidly solidified body is a supersaturated solid solution of Zr and Ti in a base metal. If this raw material is subjected to hot plastic working, not only a processed material having a desired shape is obtained but also heat energy and strain energy are sequentially or simultaneously applied to the solid body, which promotes precipitation of the second compound phase. Thus easily obtained is a heat resistant aluminum alloy in which not only the first compound phase but also the second compound phase precipitate ultrafinely in a great number in the parent phase. In addition, such an aluminum alloy can be obtained efficiently at low costs without applying aging treatment which requires a long time to precipitate the second compound phase. Of course, the second compound phase can be precipitated by heat treatment (for example, aging treatment).

(2) The higher the cooling rate of the solid body, the better. For example, it is preferred that the cooling rate is not less than 100 deg. C/sec., not less than 300 deg. C/sec., not less than 1,000 deg. C/sec., not less than 5,000 deg. C/sec., or not less than 10,000 deg. C/sec. In this case, a supersaturated solid solution of Zr and Ti, which are necessary for formation of the second compound phase, (a raw material) can be easily obtained.

[0057] This rapid solidification can be performed, for example, by atomizing, spray forming, and strip casting (roll casting, etc.). A solid body in a powdery form (atomized powder as a collective entity of atomized particles) can be obtained by atomizing. A solid body in an ingot shape can be obtained by spray forming. A solid body in a thin ribbon shape can be obtained by continuous casting.

[0058] Size of the solid body is not limited, but it is preferred that atomized particles have, for example, an average particle size of about 5 to 300 μm, and thin flakes have, for example, a thickness of about 0.05 to 1.5 mm and an area of about 5 to 8 mm square.

[0059] The raw material can be such a solid body as it is. However, it is preferred in terms of productivity, etc. to use, as a raw material, a compact or a billet formed from atomized powder (water atomized powder, gas atomized powder, water/gas atomized powder) or pulverized powder comprising thin flakes obtained by crushing or pulverizing thin ribbons.

(3) Examples of hot plastic working include extruding, forging, rolling, and sinter forging. For example, when a billet is hot extruded to obtain an extruded member (a processed member), it is preferred that billet extruding temperature is in a range of 350 to 500 deg. C or 400 to 480 deg. C. An excessively low extruding temperature is not preferable because precipitation of the second compound phase and heat resistant temperature of the aluminum alloy are insufficient, and processing force increases. On the other hand, if the extruding temperature is excessively high, coarsening of the metallic structure proceeds and heat resistance of the aluminum alloy may decrease all the more.

[0060] A billet extrusion ratio is preferably in a range of 5 to 30 or 10 to 20. If the extrusion ratio is excessively small, powder particles or pulverized flakes are insufficiently welded to each other under pressure, so desired strength or ductility cannot be obtained. If the extrusion ratio is excessively large, processing force increases so that shape forming is difficult.

[0061] It should be noted that relative density (volume density/real density) of a billet to be used for extruding or the like is not limited, but it is preferred that the relative density is not less than 60 %, not less than 70 %, not less than 80 %, not less than 85 %, or not less than 90%. If the relative density is excessively small, shape retention ability and handling ability of the billet decreases. An upper limit of the relative density is not limited, but 95 % or less is preferred in view of productivity.

<Others>

[0062] In addition to the abovementioned aluminum alloys, other aluminum alloys having softening resistance, for example, those described in Japanese Unexamined Patent Publication Nos. 2007-92117 and 2011-42861 can also be used as the substrate of the wear resistant member.

[Use Applications]

[0063] Use applications or use environments of the wear resistant member of the present invention are not limited. However, owing to its good wear resistance, the wear resistant member of the present invention is suitable as a sliding member which contacts another member or fluid (liquid or gas). Specific examples include pistons, impellers, air intake valves, connecting rods, and rotors. Since the substrate of the present invention has good heat resistance and softening resistance, the wear resistant member of the present invention is especially suitable as a member to be used in a high temperature environment. Specifically speaking, the wear resistant member of the present invention is suitable for pistons of internal combustion engines, impellers of superchargers and the like. In addition, the wear resistant member of the present invention is suitable to be used in compressors, shafts, rollers, pipes, brake cylinders, automatic transmission components, dies and molds, screws, etc.

EXAMPLES

[Production of Wear Resistant Member]

<Substrate>

[0064] An aluminum alloy of Base Material No. 11 (Al-5%Fe-1%Zr-0.85%Ti-1.5%Mg) was selected as an example from a number of aluminum alloys having good softening resistance shown in Table 1 and substrates (specimens) comprising the aluminum alloy were prepared. It should be noted that these substrates were produced by processing a raw material extruded at 430 deg. C to have a diameter of 50 mm into disks of 30 mm in diameter and 3 mm in thickness. It should be also noted that "%" means % by mass, unless otherwise specified.

<Coated Layer>

(1) Cleaning Step

[0065] These substrates were etched by an alkaline solution comprising an aqueous solution of sodium hydroxide (concentration: 50 g/L), thereby removing oxide layers formed on surfaces of the substrates (an etching step). After the etched substrates were washed with water, smut formed on the surfaces of the substrates were removed by an aqueous solution of nitric acid (concentration: 30 %) and then the treated substrates were washed again with water (a desmutting step). Thus the surfaces of the substrates were cleaned (a cleaning step).

(2) Activating Step

[0066] The cleaned substrates were further subjected to activating treatment by being immersed in a pH 11.5 aqueous sodium carbonate solution. The activating treatment was continued until standard (natural) electrode potential of the substrates shifted to -1.4 to -1.35 V (vs Ag/AgCl). It should be noted that the standard electrode potential was measured by a potentiometer by immersing the substrates after the activating treatment and an Ag/AgCl electrode in the aforementioned measurement solution. Thus, pretreatment for direct plating was performed without applying zincate treatment.

(3) Plating Step

[0067] The pretreated substrates were immersed in a plating solution at 90 deg. C for 60 minutes. The plating solution used was a commercially available electroless nickel phosphorus plating solution (Top Nicoron BL produced by Okuno Chemical Industries. Ltd.) Thus, a Ni-P plated layer was formed on a surface of each of the substrates.

(4) Heating Step (Crystallizing Step)

[0068] The plated substrates were placed in a heating furnace and heated in an atmospheric pressure environment for one hour. Heating temperature was 200 deg. C, 300 deg. C, 350 deg. C, 400 deg. C, and 450 deg. C. Thus, a plurality of specimens heated at the different heating temperatures were obtained.

(5) Comparative Examples

[0069] Also prepared were commercially available aluminum alloys (A2618, A6061) shown as Base Material Nos. C1 and C2 in Table 1. Substrates comprising these aluminum alloys were also subjected to the aforementioned treatments.

[Measurement]

(1) Hardness of Substrates and Coated Layers

[0070] The specimens heated at the different heating temperatures were respectively cut and hardness of a substrate portion and a coated layer portion in a cross section of each of the specimens was measured by a micro Vickers hardness tester (MVK-E produced by Akashi Corporation) in a room temperature state. The measurement was conducted five times under a test load of 0.245 N and a load dwell time of 20 seconds and an average of measured values was calculated. The results are respectively shown in Figs. 1 and 2. It should be noted that Fig. 2 shows hardness of the coated layers measured only about the specimens comprising Base Material No. 11, but the specimens comprising the other base materials showed similar results.

(2) Residual Stress of Coated Layers

[0071] Residual stress occurring on surfaces (Ni-P plated layers) of the specimens heated at the different heating temperatures was measured. This measurement was carried out according to the Standard Method for X-Ray Stress Measurement (The Committee on X-ray Study of Mechanical Behavior of Materials in the Society of Materials Science, Japan (1997)). Specifically, X-ray diffraction patterns of the specimens were obtained by using a sample-horizontally fixed type high power X-ray diffractometer (RINT-TTR produced by Rigaku Corporation) (X-ray source: Cu-Kα, output power: 50kV-300mA) under the parallel beam method and the iso-inclination method. Residual stress σ was calculated by the $\sin^2\psi$ method based on the X-ray diffraction patterns.

$$\sigma = K \cdot \Delta(2\theta) / \Delta(\sin^2\psi)$$

wherein:

$K = \{E \cdot \cot\theta_0 / 2(1+\nu)\} \cdot (n/180)$,
E: Young's modulus of Ni (202000 MPa),
v: Poisson's ratio of Ni (0.306)
θ_0: standard Bragg angle (diffraction angle at ψ = 0 deg.).

Results thus obtained are shown in Fig. 3. In the drawing, "+" means tensile stress and "-" means compressive stress.

[Evaluation]

(1) Hardness of Substrates

[0072] As apparent from Fig. 1, hardness of the substrates comprising Base Material No. 11 hardly changed even though heated to 450 deg. C. More specifically, hardness of the substrates was stable in a range of 160 to 170 Hv throughout the heating step, and the change was about 10 to 15 Hv at most. Additionally speaking, the substrates comprising Base Material No. 11 showed a tendency to have a higher hardness as heated at a higher temperature.

[0073] It should be noted that the substrate after subjected to the plating step and then heated at 400 deg. C had a hardness (a residual hardness) of 165 Hv, which is almost the same as residual hardness of the aluminum alloy as a single substance of Base Material No. 11 shown in Table 1.

[0074] On the other hand, hardness of the substrates comprising Base Material Nos. C1 and C2 rapidly decreased after heated to 200 deg. C or more. Hardness (residual hardness) of the substrates after heated at 400 deg. C was smaller than 80 Hv. In any case, the substrates comprising Base Material Nos. C1 or C2 after heated at 400 deg. C had residual hardness of less than 120 Hv or less than 100 Hv.

(2) Hardness of Coated Layers

[0075] As apparent from Fig. 2, hardness of the (electroless) Ni-P plated layers formed on the surfaces of the substrates in the plating step was almost constant around 500 Hv until 200 deg. C.

[0076] However, after heated above 200 deg. C, hardness of the Ni-P plated layers rapidly increased. Hardness after heated at 300 deg. C was as high as 1000 Hv, hardness after heated at 350 deg. C was as high as 1180 Hv and hardness after heated at 400 deg. C was as high as 1300 Hv.

[0077] Reason why hardness of the Ni-P plated layers thus rapidly changed after heated above a predetermined temperature is believed to be that structure of the Ni-P plated layers changed. Specifically, the reason is assumed that the Ni-P plated layers changed from an amorphous state to a crystal state (crystalline Ni-P layers). This is apparent from residual stress measurement results mentioned below.

(3) Crystallinity and Residual Stress of Coated Layers

[0078] When the surfaces of the Ni-P plated layers before and after heated at 200 deg. C were measured using X-rays as mentioned above, X-ray diffraction peaks were broad, which indicates that both the Ni-P plated layers were amorphous. This is demonstrated by X-ray diffraction images of the Ni-P plated layers shown in Fig. 4. On the other hand, when the Ni-P plated layers after heated at 350 deg. C, 400 deg. C, or 450 deg. C were measured, clear X-ray diffraction peaks appeared, which demonstrates that all the Ni-P plated layers were crystalline. Especially after heated at 400 deg. C or more, strong diffraction peaks of Ni and Ni_3P were observed.

[0079] Moreover, as apparent from Fig. 3, high compressive residual stress of 900 to 1200 MPa occurred on the surfaces of these Ni-P plated layers, and compressive residual stress increased in proportion to heating temperature. For example, when one of the Ni-P plated layers was heated at 400 deg. C, high compressive residual stress of 1017 (MPa) occurred. It should be noted that residual stress on the surfaces of the Ni-P plated layers having broad X-ray diffraction peaks could not be precisely evaluated by the aforementioned method. Therefore, for reference, residual stress on the surface of the Ni-P plated layer before heated was measured using a Brenner-Senderoff's Contractometer type electrodeposition stress measuring device, it was found that the surface is under tensile residual stress (reference value: 12 MPa). (Reference document: A. Brenner and S. Senderoff; plating, 36, 810, (1949)).

[Observation]

[0080]

(1) Electroless nickel phosphorus plating was applied to substrates comprising the aluminum alloy base materials of Base Material Nos. 11 and C3 (A1050) and having a plate shape of 10 x 70 x 1 mm by the aforementioned method. Photographs showing appearance of the specimens are respectively shown in Figs. 5A and 5B. Both the specimens were not heated after plated.

(2) As apparent from Fig. 5A, in a case of the specimen of Fe-containing Base Material No. 11, peeling off or swells were not observed on a plating surface and a uniform Ni-P plated layer was formed with high adhesion.

[0081] On the other hand, as apparent from Fig. 5B, in a case of the specimen of substantially Fe-free Base Material No. C3, swells were generated on a plating surface and a Ni-P plated layer poorly adhered.

[0082] Reason why a difference was generated between these Ni-P plated layers is assumed that the base materials had different element compositions. Base Material No. 11 contains about 5 % of Fe, but Base Material No. C3 is pure aluminum for industrial use and is substantially free of Fe as impurities (Fe: 0.40 % or less/JIS).

[0083] In a case of the specimen comprising Base Material No. 11, it is assumed that Fe was exposed to a surface by the cleaning step and the activating step and the surface served as a catalyst, so a Ni-P plated layer having high adhesion was formed. In contrast, in a case of the specimen comprising Base Material No. C3, it is assumed that even after the cleaning step and the activating step, Fe was not exposed to the surface and the base material in itself did not exhibit a catalytic action, so a Ni-P plated layer poorly adhered. Therefore, when a substrate is prepared through the activating step, it can be said that upon employing an aluminum alloy containing Fe, Ni, Pd, Mn, Co or the like, which has catalytic activity, as the substrate, a wear resistant member having a coated layer with high adhesion can be obtained.

[Wear Resistance]

[0084] In order to evaluate wear resistance of the Ni-P plated layers formed on the aluminum alloy substrates, three kinds of specimens shown in Table 2 were prepared by using Base Material No. 11 shown in Table 1. These specimens were subjected to a ball-on-disk test. The ball-on-disk test was carried out by keeping a ball (JIS SUJ2) in contact with a surface to be evaluated (a sliding surface) of each of the specimens with a constant normal load of 5 N applied to the ball, and rotating each of the specimens. In this case, sliding speed of each of the specimens with respect to the ball was 20 cm/s and sliding distance was 600 m. Moreover, this test was carried out without any lubricant in the air at room temperature.

[0085] Wear track depth obtained by measuring a surface of each of the specimens after the test by a surface roughness meter is also shown in Table 2. In addition, cross-sectional shapes of wear tracks of the respective specimens after the test are shown in Figs. 6A to 6C. It should be noted that the Ni-P plated layers before the ball-on-disk test had a thickness of 10 μm.

[0086] As apparent from these, it was confirmed that Specimen No. 1, which comprised a substrate having a sufficient residual hardness and a coated layer formed on the substrate and comprising a Ni-P plated layer subjected to high temperature treatment, was hardly worn away and exhibited high wear resistance. In contrast, the specimens except Specimen No. 1 were deeply worn away even on a substrate side. It is apparent from these results that the wear resistant member of the present invention comprising the substrate and the coated layer exhibited good wear resistance owing to a synergistic action of good residual hardness of the substrate comprising the aluminum alloy and thermal hardening characteristics of the Ni-P plated layer.

[Substrate Production]

[0087] Aluminum alloys (base materials) suitable for the aforementioned substrate can be obtained, for example, as follows. Molten aluminum alloys having composition shown in Table 1 were prepared (a molten metal preparing step). These molten alloys were sprayed in a vacuum atmosphere, thereby obtaining air atomized powders (solid bodies) (a solidifying step). Particles of the obtained air atomized powders (atomized particles) were sieved, thereby preparing atomized powders having a particle size of 150 μm or less. Note that a relation between size of powder particles obtained by air atomizing and cooling rate is known. Therefore, it can be said that the aforementioned atomized powders comprised particles rapidly solidified at a cooling rate of 10^4 deg. C/sec. or more.

[0088] The atomized powders were compacted by cold isostatic pressing (CIP), thereby obtaining extrusion billets (raw materials) having a size of 40 mm in diameter and 40 mm in length and a relative density of 85 %.

[0089] The extrusion billets were charged in a container of an extruder (not shown) . Then the extrusion billets were heated to 430 deg. C by a heater attached to the container and then extruded, thereby obtaining (solid-core) rods (processing materials) of 12 mm in diameter and 400 mm in length (a hot plastic processing/processing step). An extrusion ratio (a ratio of a cross sectional area of each raw material to a cross sectional area of each processing material) was 11.1. Samples were taken out of the thus obtained aluminum alloy rods and subjected to the following measurements.

[Measurement]

(1) Strength and Ductility

[0090] A tensile test was performed by using specimens cut out from the respective samples in order to measure strength and ductility at room temperature and strength at 300 deg. C (without preheating) . Results are also shown in Table 1. It should be noted that the tensile test was performed according to JIS Z 2241. Strength shown in Table 1 is breaking strength, and ductility is an elongation rate of a distance between two reference points in a period from a start of the test to fracture.

(2) Measurement of Residual Hardness (Softening Resistance)

[0091] Residual hardness of the respective specimens (hardness at room temperature of the specimens after heated at a high temperature) was also measured. Specifically, the specimens were held in an atmospheric environment at 400 deg. C for 10 hours, cooled to room temperature, and then measured for Vickers hardness. The Vickers hardness measurement was carried out in a room temperature environment by a Vickers hardness tester under a load of 0.98N and a load dwell time of 20 seconds.

[Evaluation of Substrates]

[0092] As apparent from Table 1, all the aluminum alloys containing proper amounts of Fe or the like exhibited not only good initial characteristics in a room temperature state but also good high temperature characteristics. Especially with an increase in Fe content, high temperature strength tended to increase. Moreover, as the aluminum alloys contain a more proper amount of Zr or Ti, the aluminum alloys had better high temperature strength and softening resistance and maintained sufficient residual hardness even after heated to 400 deg. C.

[Table 1]

Base Material No.	COMPOSITION (mass %) (Remainder: Al)					CHARACTERISTICS			
						INITIAL		HEAT RESISTANCE	
	Fe	Zr	Ti	Mg	Zr/Ti (by mass)	TENSILE STRENGTH (ROOM TEMP.) (MPa)	ELONGATION (ROOM TEMP.) (%)	RESIDUAL HARDNESS (400°C→ROOM TEMP.) (Hv)	TENSILE STRENGTH (300°C) (MPa)
1	3	1	0.85	1.5	1.18	475	9	148	180
2	4	0.7	0.6	1.5	1.17	480	9	150	185
3	4	1	0.85	0	1.18	460	9	148	178
4	4	1	0.85	1.5	1.18	500	8	152	215
5	4	1.5	1	1	1.50	520	8	160	220
6	5	0.7	0.6	1.5	1.17	490	8	150	210
7	5	0.9	0.62	1.5	1.45	510	8.5	152	215
8	5	1.4	0.95	1.5	1.47	580	5	172	225
9	5	1	0.85	0	1.18	510	7.5	155	232
10	5	1	0.85	0.7	1.18	540	8	158	250
11	5	1	0.85	1.5	1.18	570	8	165	245
12	5	1	0.85	2	1.18	590	6.5	170	238
13	5	1.1	0.75	1.5	1.47	585	6	175	255
14	5	1.1	0.95	1.5	1.16	600	6	180	258
15	5	1.5	1	1	1.50	590	5.5	185	260
16	6	0.7	0.6	1.5	1.17	585	5	175	260
17	6	1	0.85	1.5	1.18	590	5	183	265
18	6	1.5	1	1	1.50	600	5	188	270
19	6	1.5	1	0	1.50	570	5.5	180	260
20	2.5	1	0.85	0.8	1.18	405	8.5	130	125
21	3	0.5	0.25	0.6	2.00	400	9	130	115
22	3	0.5	1	-	0.50	380	10	120	110

(continued)

Base Material No.	COMPOSITION (mass %) (Remainder: Al)					CHARACTERISTICS			
						INITIAL		HEAT RESISTANCE	
	Fe	Zr	Ti	Mg	Zr/Ti (by mass)	TENSILE STRENGTH (ROOM TEMP.) (MPa)	ELONGATION (ROOM TEMP.) (%)	RESIDUAL HARDNESS (400°C→ROOM TEMP.) (Hv)	TENSILE STRENGTH (300°C) (MPa)
23	3	1	1	-	1.00	405	7	130	140
24	4	0.5	1	-	0.50	385	8	125	120
25	4	2	-	-	∞	390	1.5	140	150
26	4	1	1	-	1.00	450	6.5	135	140
27	5	0.6	0.3	1.5	2.00	460	6	145	155
28	5	1	1	0	1.00	470	5	140	165
29	5	0.5	1	-	0.50	420	7	135	140
30	5	2	-	-	∞	440	1	150	158
31	6	0.6	0.3	1.5	2.00	480	6	155	165
32	6	0.8	1	-	0.80	480	8	150	165
33	6	-	0.85	-	0.00	400	7.5	135	140
34	6	-	1	1.5	0.00	430	6	145	150
35	7	1	0.85	1.5	1.18	600	3	200	280
36	7	-	1	1.5	0.00	480	4	170	225
C1	A2618 (JIS)					440	10	80	54
C2	A6061 (JIS)					310	17	45	35
C3	A1050 (JIS)					150	18	40	25

*In all of Base Material Nos. 1 to 36, content of impurities (Si, Cu, Mn, Cr, etc.) was 0.25 % or less.

[Table 2]

SPECIMEN NO.	Ni-P PLATED LAYER	HEATING STEP	HARDNESS (Hv)		WEAR TRACK DEPTH (μm)
			SUBSTRATE (Base Material No.11)	COATED LAYER (Ni-P Plated Layer)	
1	+	Heating at 400 deg. C	**165**	**1300**	**3**
2	+	-		**500**	**38**
3	-	-		**-**	**55**

Claims

1. A wear resistant aluminum alloy member, comprising:

   a substrate comprising an aluminum alloy, and
   a coated layer coating at least part of a surface of the substrate, wherein:

      the aluminum alloy has a residual hardness of 120 Hv or more when measured in a room temperature state after held in an atmospheric pressure environment at 400 deg. C for 10 hours; and
      the coated layer comprises a crystalline Ni-P layer comprising nickel (Ni) and nickel phosphide (Ni_3P).

2. The wear resistant aluminum alloy member according to claim 1, wherein the crystalline Ni-P layer contains 1 to 13 % by mass (hereinafter simply referred to as "%") of P when a total mass of the crystalline Ni-P layer is taken as 100 %.

3. The wear resistant aluminum alloy member according to claim 1 or 2, wherein the crystalline Ni-P layer is formed by heating an amorphous Ni-P plated layer formed on the surface of the substrate by electroless Ni-P plating.

4. The wear resistant aluminum alloy member according to any one of claims 1 to 3, wherein compressive residual stress is present in the crystalline Ni-P layer.

5. The wear resistant aluminum member according to claim 1 or 4, wherein the aluminum alloy contains 1 to 7 % of iron (Fe) when a total mass of the aluminum alloy is taken as 100 %.

6. The wear resistant aluminum alloy member according to claim 5, wherein the aluminum alloy further contains:

   0.5 to 3 % of zirconium (Zr), and
   0.5 to 3 % of titanium (Ti),

   when the total mass of the aluminum alloy is taken as 100 %.

7. The wear resistant aluminum alloy member according to claim 6, wherein the aluminum alloy further contains 0.5 to 5 % of magnesium (Mg) when the total mass of the aluminum alloy is taken as 100 %.

8. A method for producing the wear resistant aluminum alloy member according to any one of claims 1 to 7, having:

   a plating step of forming a Ni-P plated layer on the surface of the substrate by bringing the surface of the substrate in contact with an electroless Ni-P plating solution; and
   a crystallizing step of crystallizing the Ni-P plated layer by heating the Ni-P plated layer.

9. The method for producing the wear resistant aluminum alloy member according to claim 8, having, before the plating step, a pretreatment step comprising an activating step of activating the surface of the substrate by bringing the surface of the substrate in contact with a treatment solution, or a zincate step of applying zincate treatment to the surface of the substrate.

10. The method for producing the wear resistant aluminum alloy member according to claim 9, having, before the pretreatment step, a cleaning step of cleaning the surface of the substrate.

11. The method for producing the wear resistant aluminum alloy member according to claim 10, wherein the cleaning step comprises:

an etching step of removing an oxide layer by bringing the substrate in contact with an alkaline solution; and
a desmutting step of removing smut formed after the etching step with an acid solution.

12. The method for producing the wear resistant aluminum alloy member according to any one of claims 8 to 11, wherein the substrate comprises an aluminum alloy obtained through:

a solidifying step of obtaining a solid body by rapidly solidifying a molten alloy, and
a heat treatment step of heating the solid body.

13. The method for producing the wear resistant aluminum alloy member according to claim 12, wherein the heat treatment step is a hot working step of performing hot plastic working on the solid body.

FIG.1

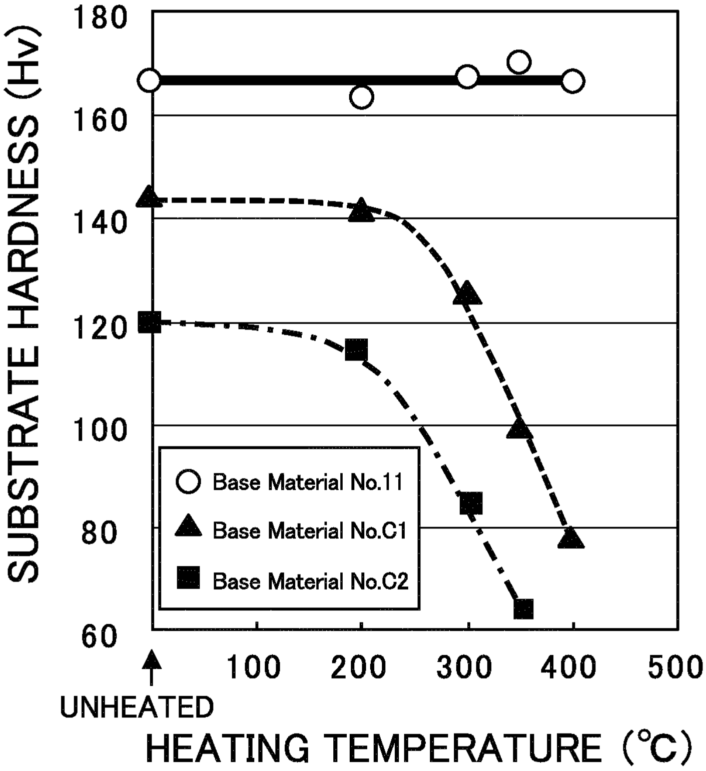

SUBSTRATE HARDNESS (Hv)
180
160
140
120
100
80
60
100
200
300
400
500
UNHEATED
HEATING TEMPERATURE (°C)
○ Base Material No.11
▲ Base Material No.C1
■ Base Material No.C2

FIG.2

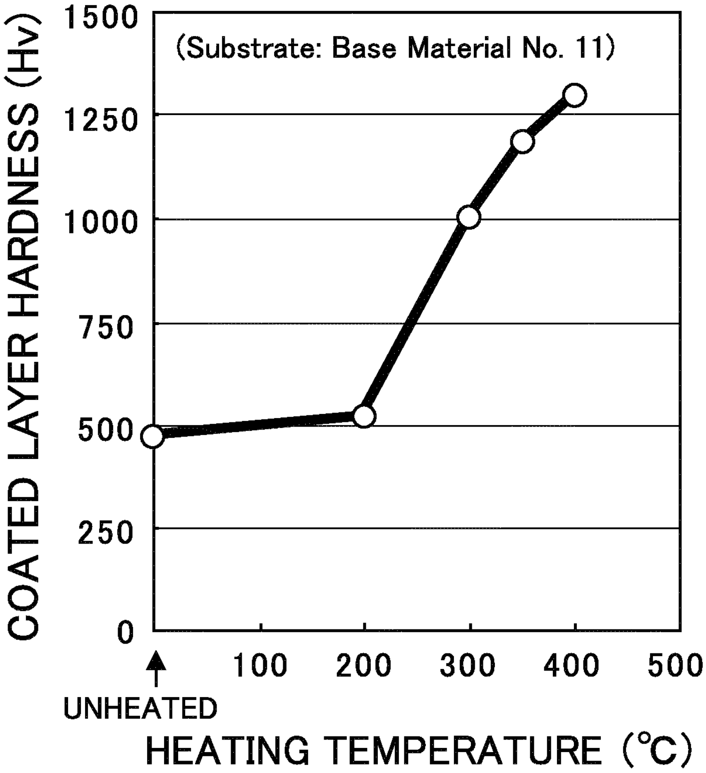

COATED LAYER HARDNESS (Hv)
1500
1250
1000
750
500
250
0
100
200
300
400
500
UNHEATED
HEATING TEMPERATURE (°C)
(Substrate: Base Material No. 11)

FIG.3

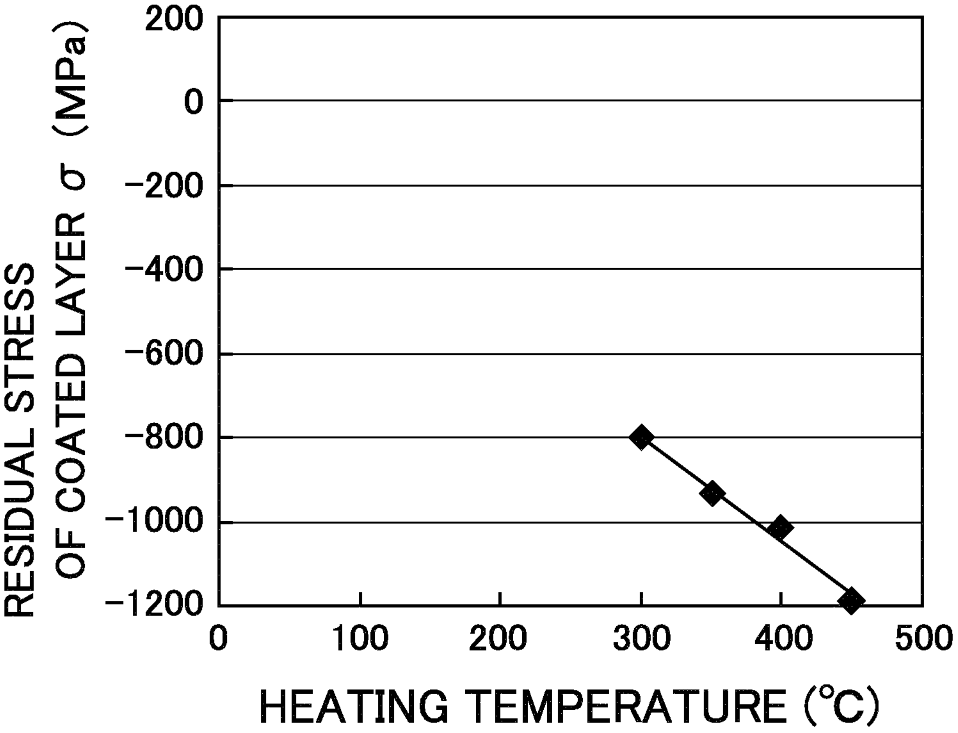

RESIDUAL STRESS
OF COATED LAYER σ (MPa)
200
0
−200
−400
−600
−800
−1000
−1200
0
100
200
300
400
500
HEATING TEMPERATURE (℃)

FIG.4

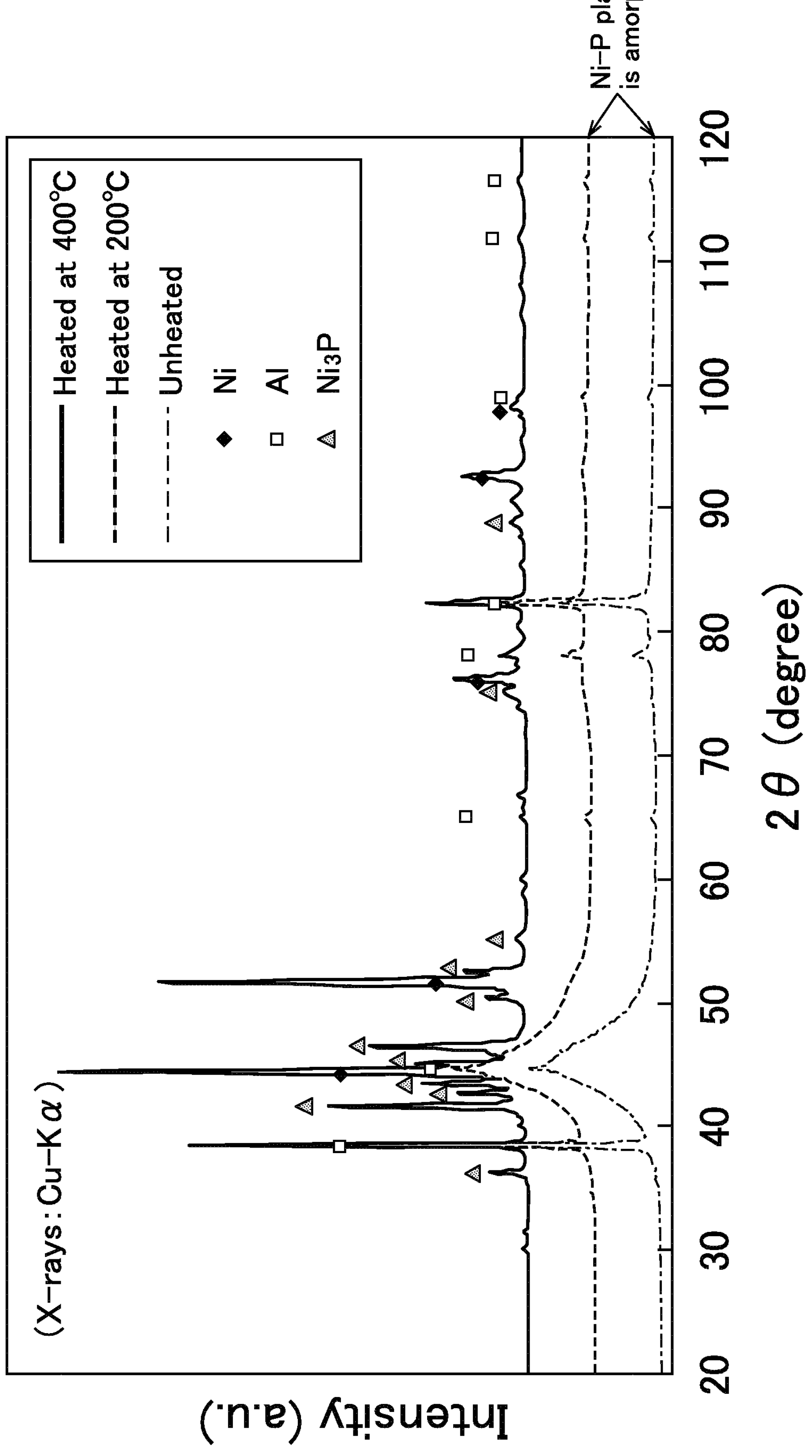
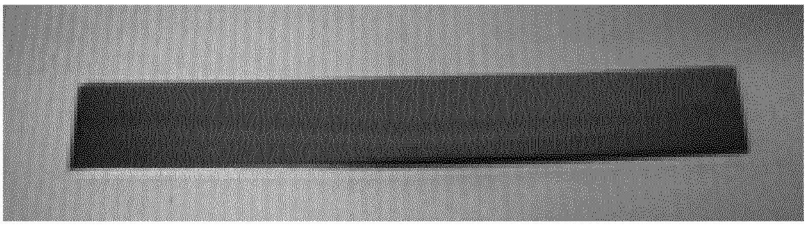
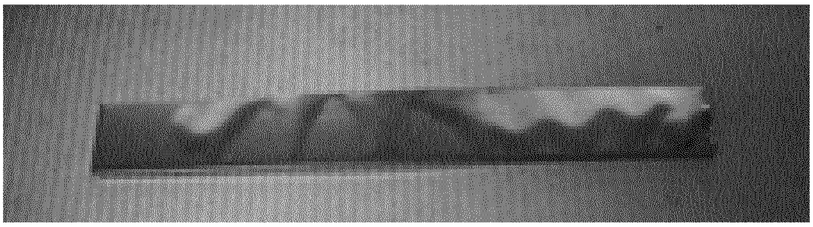

Ni–P plated layer is amorphous.
(X–rays : Cu–K α)
Heated at 400°C
Heated at 200°C
Unheated
◆ Ni
□ Al
△ Ni3P
Intensity (a.u.)
2 θ (degree)
20
30
40
50
60
70
80
90
100
110
120

FIG.5A



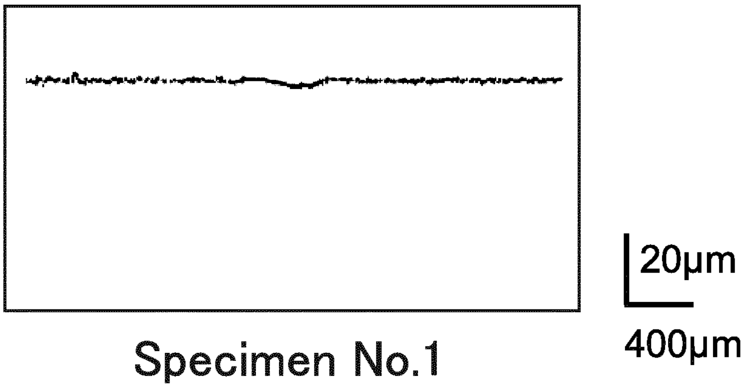
Base Material No. 11

FIG.5B



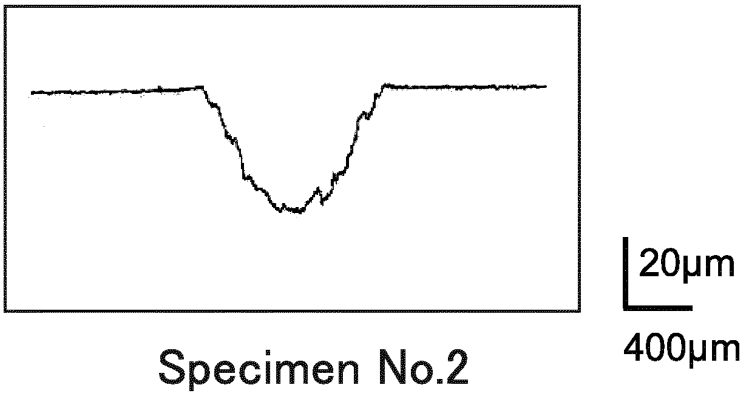
Base Material No. C3

FIG.6A



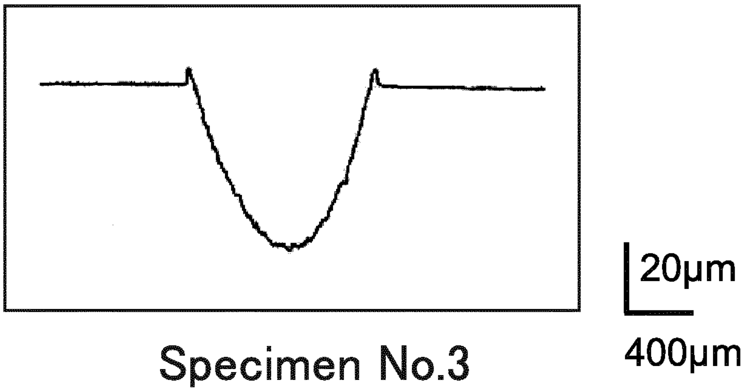
Specimen No.1

FIG.6B



Specimen No.2

FIG.6C



Specimen No.3

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2012/069872

A. CLASSIFICATION OF SUBJECT MATTER
C23C18/36(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C23C18/36

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Jitsuyo Shinan Koho	1922-1996	Jitsuyo Shinan Toroku Koho	1996-2012
Kokai Jitsuyo Shinan Koho	1971-2012	Toroku Jitsuyo Shinan Koho	1994-2012

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	JP 2974836 B2 (Honda Motor Co., Ltd.), 10 November 1999 (10.11.1999), entire text (Family: none)	1-13
Y	JP 3-138374 A (Mitsubishi Electric Corp.), 12 June 1991 (12.06.1991), entire text (Family: none)	1-13
Y	JP 2005-350686 A (National University Corporation Gunma University), 22 December 2005 (22.12.2005), claims; paragraphs [0021], [0025] (Family: none)	9-13

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search 28 August, 2012 (28.08.12)	Date of mailing of the international search report 04 September, 2012 (04.09.12)
Name and mailing address of the ISA/ Japanese Patent Office Facsimile No.	Authorized officer Telephone No.

Form PCT/ISA/210 (second sheet) (July 2009)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2012/069872

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	JP 6-323327 A (Sumitomo Light Metal Industries, Ltd.), 25 November 1994 (25.11.1994), paragraphs [0010] to [0015], [0017] to [0020] (Family: none)	9-13

REFERENCES CITED IN THE DESCRIPTION

Patent documents cited in the description

- JP 3009527 B **[0004]**
- JP 2004277784 A **[0004]**
- JP 2648716 B **[0035]**
- JP 2007092117 A **[0062]**
- JP 2011042861 A **[0062]**

Non-patent literature cited in the description

- The Committee on X-ray Study of Mechanical Behavior of Materials in the Society of Materials. *Science,* 1997 **[0019]**
- *The Committee on X-ray Study of Mechanical Behavior of Materials in the Society of Materials Science,* 1997 **[0071]**
- **A. BRENNER ; S. SENDEROFF.** *plating,* 1949, vol. 36, 810 **[0079]**