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

(11) EP 3 081 377 A1

(12) EUROPEAN PATENT APPLICATION
published in accordance with Art. 153(4) EPC

(43) Date of publication:
19.10.2016 Bulletin 2016/42

(21) Application number: **14870370.5**

(22) Date of filing: **04.12.2014**

(51) Int Cl.:
B32B 15/16 (2006.01) ***B24B 1/00*** (2006.01)
B24B 37/00 (2012.01) ***B32B 9/00*** (2006.01)
C23C 24/06 (2006.01)

(86) International application number:
PCT/JP2014/082099

(87) International publication number:
WO 2015/087771 (18.06.2015 Gazette 2015/24)

(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
Designated Extension States:
BA ME

(30) Priority: **13.12.2013 JP 2013258722**

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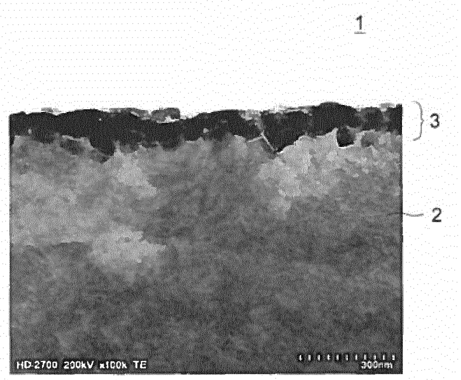
(54) ARTICLE WITH METAL OXIDE FILM

(57) Provided is an article having a metal oxide coating employing a novel configuration exhibiting both color and metallic luster. The article having a metal oxide coating disclosed herein is provided with a base material including a metal material and a metal oxide coating including a metal oxide coated onto the surface of the base material. The metal oxide coating is formed by polishing the surface of the base material, using particles composed of the metal oxide.

[Fig. 1]



Description

Technical Field

[0001] The present invention relates to an article having a metal oxide coating. The present application claims priority on the basis of Japanese Patent Application No. 2013-258722, which was filed on December 13, 2013, the contents of which are incorporated herein by reference.

Background Art

[0002] Various types of metal materials are used as base materials of electronic equipment represented by home electrical appliances, household goods, sporting goods, healthcare products, automobile exterior and interior materials, building materials and various other articles. The surfaces of these materials are subjected to various surface processing with coatings made of resin materials, ceramic materials, glass materials or metal materials and the like for the purpose of protecting the surface and imparting designability. There are heightened requirements for surface designability, in particular, in electronic equipment and automobile interior materials, and processing is required that is capable of strongly reflecting the preferences of the user. For examples, the surfaces of metal materials are typically coated using various techniques such as various types of printing technologies, chemical vapor deposition, physical vapor deposition or lamination of decorative materials.

Citation List

Patent Literature

[0003]

Patent Literature 1: Japanese Patent Application Publication No. H2-185365
Patent Literature 2: Japanese Patent Application Publication No. H4-201069
Patent Literature 3: Japanese Patent Application Publication No. H7-256555
Patent Literature 4: Japanese Patent Application Publication No. H10-036819

Summary of Invention

Technical Problem

[0004] In the surface processing of metal materials, for example, surface processing that realizes a surface design having a completely different texture from that of the metal material, or surface processing that brings out the inherent texture of the metal material, is carried out by coating with various types of materials as previously described. Known examples of surface processing that brings out the texture of the metal material include processing that removes the luster from the surface by hairline processing or blast processing, and mirrored surface polishing that enhances the glossiness of the metal by polishing the metal surface. Examples of the prior art relating to polishing metal materials are described in Patent Literature 1 to 4.

[0005] In addition, in the surface processing of metal materials, the processed article is required to realize diverse designability corresponding to the preference of the user using that article. As an example thereof, the luster of a metal material may be required to realize various colors. In addition, the luster thereof is preferably realized as that having various patina. In this manner, if it were possible to realize an article composed of metal materials having color and luster by an increasingly diverse range of configurations, in addition to naturally enhancing the designability of that article, the manner of use and applications thereof could also be expanded. This would also be preferable since it would be possible to provide articles capable of flexibly accommodating a wide range of user preferences.

[0006] With the foregoing in view, an object of the present invention is to provide an article having a metal oxide coating employing a novel configuration exhibiting both color and metallic luster.

Solution to Problem

[0007] In order to solve the problem, the article having a metal oxide coating provided by the present invention includes a base material including a metal material and a metal oxide coating including a metal oxide coated onto a surface of the base material. The metal oxide coating is formed by polishing the surface of the base material, using particles including the metal oxide (which may also be simply referred to as "metal oxide particles").

[0008] In this article having a metal oxide coating, the surface of the metal base material is coated directly with a metal oxide coating without having a binder component and the like interposed there between. The metal oxide coating is formed by embedding metal oxide particles into the surface of the metal base material by polishing. Even though the surface of the metal material is coated with metal oxide particles in this manner, an article can be realized that is provided with metallic luster. In addition, the particles comprising a metal oxide can be densely and uniformly embedded in the surface of the metal base material by using a polishing technology. A desired color and unique patina can be imparted to that metallic luster corresponding to the physical properties of the metal oxide particles. Namely, the article having a metal oxide coating disclosed herein realizes color and metallic luster by employing a configuration not previously found in the prior art.

[0009] Furthermore, the term "polishing" in the present description refers to the operation of placing metal oxide particles on the surface of the base material and moving both components relatively in a direction parallel to the surface of a substrate, and does not necessarily refer to an operation carried out for the purpose of smoothing the surface of a base material.

[0010] In a preferred aspect of the article having a metal oxide coating disclosed herein, the mean primary particle diameter of the particles including a metal oxide is 10 nm to 1 μm. As a result of employing this configuration, an article is provided in which the thickness of the metal oxide coating is more uniform and the effects of the color and metallic luster are expressed more effectively.

[0011] In a preferred aspect of the article having a metal oxide coating disclosed herein, the base material includes a metal material having a Brinell hardness of 10 to 200. According to a base material employing this configuration, the metal oxide particles can be retained on the surface in a more strongly adhered state. As a result, the glossy appearance of the base material can be enhanced and designability can be maintained over a long period of time.

[0012] In a preferred aspect of the article having a metal oxide coating disclosed herein, the metal oxide particles contain one or more types of oxides selected from the group consisting of zirconium oxide, cerium oxide and aluminum oxide.

[0013] According to this configuration, luster and color of different patina can be realized easily according to the physical properties of each metal oxide particle, and an article having a metal oxide coating is provided that has a diverse range of designability.

[0014] In a preferred aspect of the article having an oxide coating disclosed herein, the base material is aluminum or an aluminum alloy. According to this configuration, in addition to providing a more glossy appearance, an article having a metal oxide coating is provided that is lightweight and has ample processability. For example, an article having a metal oxide coating is provided that has an extremely high sense of quality while also demonstrating a rich luster.

Brief Description of Drawings

[0015] Fig. 1 is an electron micrograph depicting a cross-section of an article having a metal oxide coating according to one embodiment obtained with a scanning electron microscope (SEM).

Description of Embodiments

[0016] The following provides an explanation of preferred embodiments of the present invention. Furthermore, matters necessary for implementing the present invention other than those specifically referred to in the present description may be understood to be design matters for a person with ordinary skill in the art based on the conventional art in the relevant feld. The present invention can be implemented based on the contents disclosed in the present description and common general technical knowledge in the subject field.

[0017] In addition, although dimensional relationships (such as length, width or thickness) in the drawings represent the approximate external characteristics of the article having a metal oxide coating of the present invention, they do not necessarily reflect the actual dimensional relationships of the article.

[Configuration of Article having Metal Oxide Coating]

[0018] Fig. 1 is a cross-sectional view in the vicinity of the surface of an article having a metal oxide coating according to one embodiment obtained by observing with a scanning electron microscope (SEM). As shown in Fig. 1, an article having a metal oxide coating 1 disclosed herein is essentially provided with a base material 2 including a metal material, and a metal oxide coating 3 including a metal oxide that coats the surface of the base material 2. This metal oxide coating 3 is formed by polishing the surface of the base material 2 using particles including a metal oxide.

[Base Material]

[0019] There are no limitations on the metal material that comprises the base material 2, and can be various types of metals alone (namely, pure metals) or metal oxides. Furthermore, oxides as referred to here include substances composed of two or more types of elements that demonstrate metallic properties, and may be mixed in the form of a solid solution, intermetallic compound or mixture thereof. Specific examples of metal materials that includes the base material 2 include typical elements such as Mg, Sr, Ba, Zn, Al, Ga, In, Sn or Pb, transition metal elements such as Sc, Y, Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W, Mn, Fe, Co, Ni, Cu, Ag, Re, Os, Ir, Pt or Au, lanthanide series elements such as La, Ce, Pr, Nd, Sm, Eu, Gd, Yb, Er or Lu, and alloys including these elements and one or more types of other elements. These metal materials are naturally allowed to contain unintended elements in the form of unavoidable impurities and the like.
[0020] Although not necessarily limited thereto, if the base material 2 includes a metal material having a Brinell hardness (HBW) of 10 to 200, metal oxide particles can be easily and securely immobilized on the surface thereof, thereby making this preferable. This is particularly preferable for immobilizing metal oxide particles on the surface thereof using, for example, a polishing technology to be subsequently described. If the Brinell hardness is 150 or less, in addition to facilitating immobilization of the metal oxide particles, the metal oxide particles and base material 2 can be securely adhered, thereby making this preferable. On the other hand, if the base material 2 is excessively soft, its application may be limited or the possibility may occur of the strength required to retain the metal oxide particles conversely weakening, thereby making this undesirable. From these viewpoints, Brinell hardness is preferably 15 or more and more preferably 20 or more.
[0021] Specific examples of metal materials that satisfy this level of Brinell hardness include aluminum (20), aluminum alloys such as 1000 series aluminum alloy (15-25), 2000 series aluminum alloy (90-140), 3000 series aluminum alloy (20-50), 4000 series aluminum alloy (100-200), 5000 series aluminum alloy (20-100), 6000 series aluminum alloy (50-100) or 7000 series aluminum alloy (80-160), copper (24), brass (90-100), bronze (40-100), cast iron (150-200), chrome steel (50-187), zirconium steel (50-140) and S30C carbon steel for machine structural use (130-200). Furthermore, the numerical values in parentheses shown after the names of the metal materials above indicate typical Brinell hardness numbers of the metal materials.
[0022] Furthermore, in the present description, "Brinell hardness" refers to the value measured in compliance with "Brinell hardness test - Test method" defined JIS Z 2243:2008.
[0023] Furthermore, high reflectivity of the base material 2 with respect to visible light (such as light having a wavelength of about 360 nm to 830 nm, and typically 400 nm to 760 nm) is also preferable from the viewpoint of enhancing designability of the glossy surface thereof. Although reflectance cannot be defined uniformly since it varies according to the target light wavelength, examples of materials having high reflectance include gold, silver, copper, aluminum, platinum and iron. The use of, for example, a metal material that reflects visible light of a prescribed wavelength region for the base material 2 allows the obtaining of metallic luster of a prescribed color. In addition, the use of, for example, a metal material that equally reflects visible light of all wavelength regions for the base material 2 allows the obtaining of so-called colorless metallic luster, while also making it possible to effectively take advantage of optical effects attributable to the metal oxide coating 3 to be subsequently described, thereby making this preferable. Typical examples of metal materials provided with this colorless or nearly colorless metallic luster include silver, aluminum and aluminum alloy. The base material 2 is preferably composed of aluminum or aluminum alloy when comprehensively considering processing and other applications, availability, cost, reflectance, hardness and other physical properties.
[0024] There are no particular limitations on the shape (external form) of the base material 2, and a metal material of any desired shape can be considered for use as the base material 2. Furthermore, in the article having a metal oxide coating 1 disclosed herein, the metal oxide coating 3 is preferably produced by polishing. Although not necessarily limited thereto, at least a portion of the base material 2 used to produce the article having a metal oxide coating 1 is preferably provided with a flat surface in consideration of ease when forming the metal oxide coating 3. The surface is preferably provided with flatness of a degree, for example, that allows the base material 2 to realize a so-called mirrored surface. Here, a mirrored surface can be a surface in which, for example, surface roughness Ra is preferably 20 nm or less and more preferably 10 nm or less. As a result of realizing the article having a metal oxide coating 1 using the base material 2 having such flatness, reflection of light on the base material surface of the article having a metal oxide coating I can be preferably utilized in the form of gloss, thereby making this preferable. In addition, although unable to be uniformly defined as a result of varying according to material quality (such as Brinell hardness) and the like of the base material 2, in addition to facilitating the realization of a securely adhered state between the base material 2 and metal oxide particles in the article having a metal oxide coating 1, light entering the article 1 can be inhibited from being excessively scattered. As a result, metallic luster can be preferably maintained even after the metal oxide coating 3 has been formed on the surface of the base material 2.
[0025] Furthermore, "surface roughness Ra" in the present description refers to arithmetic average roughness Ra, which is defined as a roughness parameter of the properties of a surface in JIS B 0601:2013. This surface roughness Ra can be measured by using a commercially available, non-contact surface profile measuring instrument that uses a

laser and the like.

[0026] On the other hand, there are no particular limitations on the dimensions or thickness of the base material 2, and for example, a base material 2 of a desired shape can be used within a range that allows polishing. Although the base material 2 can typically be a plate, it is not limited thereto. In addition, the plate may also be processed into an article of a prescribed shape, for example. In addition, even in the case of a plate, the plate is not limited to a single-layer material composed of a single layer, for example, but rather may also be a laminated material and the like having a structure of two layers or three layers or more. In the case the base material 2 is a laminated material, the uppermost surface on which the metal oxide coating 3 is formed is preferably composed of aluminum or an aluminum alloy as previously described. Moreover, the surface of the base material 2 may be curved or flat, and a flat surface may be provided in the form of protrusions on at least a portion of the curved or flat surface. Furthermore, in the case the surface is provided in the form of flat protrusions as described above, the metal oxide coating 3 can be easily provided only on the protrusions, thereby also making this preferable. In this case, the protrusions can be formed into a desired pattern, for example.

[Metal Oxide Coating]

[0027] The surface of the base material 2 is covered with the metal oxide coating 3. The presence of this metal oxide coating 3 enables the article having a metal oxide coating 1 disclosed herein to be provided with a unique design while also having a diverse range of color and luster.

[0028] The metal oxide coating 3 is typically composed by gathering metal oxide particles. Although the metal oxide particles may compose a coating by being mutually connected, it is not necessarily required that all metal oxide particles to be integrally connected. For example, the metal oxide particles may be present separately on the surface of the base material 2 without being mutually connected. As a result of each of the metal oxide particles being immobilized on the surface of the base material 2 by being securely adhered thereto, the metal oxide particles are able to collectively constitute a coating. Furthermore, even in the case a plurality of the metal oxide particles are mutually connected, as shown in Fig. 1, for example, the metal oxide particles composing the metal oxide coating 3 can each be confirmed, through observations with an electron microscope and the like, to be separate, independent particles. For example, particle boundaries between closely connected particles can be determined in SEM images by using different contrast levels. With respect to this point, this metal oxide coating 3 can be clearly distinguished from natural oxide coatings formed as a result of a base material surface being nearly uniformly oxidized.

[0029] In addition, the metal oxide coating 3 can be composed by laminating one layer and/or two or more layers of the metal oxide particles on the surface of the base material 2. Depositing roughly about one layer of the metal oxide particles on the surface of the base material 2 is preferable for securely immobilizing the metal oxide particles on the base material 2. Furthermore, the metal oxide particles may be deposited in two or more layers (typically two to three layers) on the metal oxide coating 3 within a range that allows the metal oxide particles to be securely immobilized on the surface of the base material 2.

[0030] Furthermore, the metal oxide particles are provided by being directly adhered (fixed) to the surface of the base material 2 without having a resin or other binder interposed there between. The mechanism of this adhesion is not necessarily required to be identified. However, although not limited thereto, this adhesion can be realized by, for example, surface activity of fine metal oxide particles together with surface activating action of the base material 2 attributable to polishing. A state in which contact is made by a weak binding force such as that due to electrostatic attraction is excluded from adhesion as referred to here. This adhesion can include a state in which the metal oxide particles are mechanically fixed to the base material 2. More preferably, at least a portion of the metal oxide particles are in a state of being anchored in the surface of the base material 2. In addition, the interface between the metal oxide particles and the base material 2 can be in a state of generally close contact. Namely, the interface between the metal oxide particles and the base material 2 is formed into surface irregularities that match the shape of the metal oxide particles. Due to such irregularities formed in the interface, the metal oxide particles and the base material 2 fit (engage) together, such as when the interface thereof intermingles three-dimensionally, and the metal oxide particles can be securely immobilized on the base material 2. As a result of the metal oxide particles being adhered and immobilized on the base material 2 in this manner, the metal oxide particles can be inhibited from separating from the base material 2 even when, for example, the article 1 is used over a long period of time.

[0031] There are no particular limitations on the composition of the metal oxide particles, and may be particles composed of various types of metal oxides. Examples of metal elements that compose these metal oxides include one type or two or more types of elements selected from metalloid elements such as B, Si, Ge, Sb or Bi, typical metal elements such as Mg, Ca, Sr, Ba, Zn, Al, Ga, In, Sn or Pb, transition metal elements such as Sc, Y, Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W, Mn, Fe, Co, Ni, Cu, Ag, Re, Os, Ir, Pt or Au, and lanthanide elements such as La, Ce, Pr, Nd, Sm, Eu, Gd, Yb, Er or Lu. Among these, an oxide containing one type or two or more types of elements selected from Zr, Ce, Al, Ti, Cr, Mn and Zn is preferable for the metal oxide.

[0032] Furthermore, the metal oxide coating 3, namely the metal oxide coating that composes the metal oxide particles, can be selected and used that has a desired refractive index from the viewpoint of coloring of the article 1 having a metal oxide coating, for example. Although there are no particular limitations thereon, a metal oxide having a high refractive index is preferable in order to preferably control the color of the article I having a metal oxide coating, for example. The refractive index of the metal oxide that composes the metal oxide particles is preferably 1.5 or more, more preferably 2 or more and even more preferably 2.3 or more. Specific examples of metal oxides having a comparatively high refractive index include zirconium oxide (ZrO_2), cerium oxide (CeO_2), aluminum oxide (Al_2O_3), titanium oxide (such as TiO, Ti_3O_5 or TiO_2), tantalum pentoxide (Ta_2O_5), niobium oxide (Nb_2O_5) and hafnium oxide (HfO_2). Furthermore, when considering esthetics with respect to visible light, this metal oxide is preferably transparent, and more preferably colorless and transparent, in monocrystalline form. From these viewpoints, specific examples of preferable metal oxides include (ZrO_2), cerium oxide (CeO_2), aluminum oxide (Al_2O_3), and titanium oxide (such as TiO, Ti_3O_5 or TiO_2).

[0033] In addition, there are no particular limitations on the geometrical shape (external shape) of the metal oxide particles, and may have various shapes, ranging from, for example, a spherical shape to an irregular shape. Furthermore, a shape other than a spherical shape (such as a perfectly spherical shape) is preferable from the viewpoint of being able to securely adhere the metal oxide particles to the base material 2. As a typical example thereof, an external shape is preferable that reflects the crystal system of the metal oxide that composes the metal oxide particles. An external shape that reflects the crystal system can be realized by, for example, producing metal oxide particles without subjecting to any particular spheroidizing treatment, producing the metal oxide particles by going through process for allowing sufficient crystal growth, or producing the metal oxide particles by crushing. The metal oxide particles easily become anchored in the surface of the base material 2 due to the presence of crystal planes, ridges, angles or corners in the metal oxide particles, and strong engagement can be realized more easily. In addition, the metal oxide particles 3 being in the form of highly crystalline crystal particles is also preferable from the viewpoint of further enhancing the optical effects to be subsequently described.

[0034] The mean primary particle diameter of the metal oxide particles can be 10 nm to 1 μm. If the mean primary particle diameter is less than 10 nm, the contribution of the metal oxide particles to the base material 2 diminishes easily, and it can be difficult to provide color diversity through optical effects, thereby making this undesirable. From this viewpoint, the mean primary particle diameter of the metal oxide particles is more preferably 30 nm or more and even more preferably 50 nm or more. For example, mean primary particle diameter can be 100 nm or more. However, if the mean primary particle diameter exceeds 1 μm, it becomes difficult to maintain the smoothness of the surface of the article having a metal oxide coating 1, thereby making this undesirable. In addition, if the metal oxide particles are comparatively large, it can become difficult to immobilize the metal oxide particles on the base material 2 without using a binder component, thereby also making this undesirable. From these viewpoints, the mean primary particle diameter of the metal oxide particles is preferably 800 nm or less and more preferably 500 nm or less.

[0035] Mean primary particle diameter of the metal oxide particles can be determined by, for example, observing with an electron microscope.

[0036] The specific procedure for determining mean primary particle diameter includes, for example, obtaining an image of an arbitrary cross-section of the article having a metal oxide coating 1 using a suitable observation means such as an electron microscope, determining the equivalent circle diameter of a prescribed number of metal oxide particles (such as 100), and obtaining mean primary particle diameter by calculating the arithmetic mean value thereof.

[0037] Furthermore, although there are no strict limitations on the average thickness of the metal oxide coating 3 composed of the metal oxide particles as previously described, the overall average thickness is preferably within the range of about 10 nm to 1 μm and more preferably 30 nm to 600 nm. The optical path of light that is irradiated onto the article having a metal oxide coating 1 and passes through the metal oxide coating 3 is determined based on the thickness and so forth of the metal oxide coating 3. Color imparted to the article having a metal oxide coating I and the effects thereof can be changed in various ways by adjusting the optical path to a desired value.

[0038] Furthermore, average thickness of the metal oxide coating 3 can be determined visually or by image analysis based on observations, for example, with an electron microscope. For example, images of the cross-section of the metal oxide coating can be observed with a transmission electron microscope, and the value obtained by visually measuring about 3 to 10 locations per image using a scale bar can be used for coating thickness.

[0039] Furthermore, unavoidable formed products and the like are permitted to be interposed at the interface between the metal oxide particles and the base material 2. These products can include, for example, a metal oxide coating formed from metal materials that compose the base material 2 and other unintended reaction products. The inclusion of such products at the interface between the metal oxide particles and the base material 2 can be an allowable implementation of the article having a metal oxide coating 1 disclosed herein.

[Designability]

[0040] The article having a metal oxide coating 1 having the above-mentioned configuration is able to express metallic luster attributable to the base material 2 thereof despite providing the metal oxide coating 3 on the surface thereof. In the case of, for example, viewing the surface of the article having a metal oxide coating 1 from a direction perpendicular to that surface (namely, viewing from directly in front of the surface), the appearance is primarily roughly the same as that of the base material 2 alone. However, in the case of viewing the article having a metal oxide coating 1 from a direction at an angle to the surface thereof, the metallic luster can primarily be accompanied by red, orange, yellow, green, blue, purple and mixed colors thereof and/or white color (hue). Furthermore, metallic luster can also be accompanied by such color even in the case of viewing from the so-called direction directly in front of the surface depending on the configuration of the article having a metal oxide coating 1. This color is able to impart a unique patina based on the configuration of the metal oxide coating 3, which can be said to be a collection of metal oxide particles. For example, a more subdued luster can be obtained, in which the so-called sparkling metallic appearance is diminished, as is observed in color plated articles and the like.

[0041] The article having a metal oxide coating 1 is able to realize an elegant and brilliant appearance not found in the prior art as previously described by adding optical effects in addition to the configuration of the article having a metal oxide coating 1. In addition, the aspect of this appearance can be subtly changed according to the angle at which the article having a metal oxide coating 1 is viewed and conditions at that location such as the light source. Namely, the degree of coloring (such as color intensity), degree of brightness or color tone and the like change subtly. This article having a metal oxide coating 1 can have superior designability and a high level of esthetics while demonstrating unique color and luster not found in the prior art.

[0042] Designability of the article having a metal oxide coating 1 as described above can be evaluated and managed based on, for example, the indices indicated below.

<Glossiness>

[0043] The greatest characteristic relating to designability of metal materials is the generation of metallic luster by reflecting light. Metallic luster provided based on the base material 2 can also be evaluated according to glossiness, for example, in the case of the article having a metal oxide coating 1 disclosed herein. This glossiness can be measured based on, for example, the methods used to measure specular glossiness described in JIS Z8741:1997. The evaluation target in the form of the article having a metal oxide coating 1 can be evaluated as to whether or not the coating is provided with suitable glossiness corresponding to the application or required designability thereof based on this glossiness. Furthermore, surface reflection properties of the article having a metal oxide coating 1 can be evaluated by, for example, determining the commonly known bidirectional reflectance distribution function (BRDF).

<Color>

[0044] The coloring (color) of the surface of the article having a metal oxide coating I disclosed herein can be evaluated and managed, for example, by using the criteria of hue, lightness and saturation. The color of the article having a metal oxide coating 1 disclosed herein that is evaluated includes the tint of the metal material per se that composes the base material 2 and tint expressed by optical effects realized by the metal oxide coating 3. This evaluation can be carried out based on a sensory evaluation by panelists or the specification method of object colors defined in JIS Z 8730:2009. A sensory evaluation by panelists enables a more realistic evaluation by including weighting in consideration of such factors as the characteristics and application of the evaluated article. In addition, evaluation by color specification enables a more objective evaluation since color can be expressed numerically, for example, as the tristimulus values of hue, lightness and saturation and then converted to a uniform color space (UCS).

[0045] Furthermore, although it is not necessary here to elucidate the reasons for the article having a metal oxide coating I bringing about the unique color and luster described above, optical effects like those described below, for example, are thought to be demonstrated.

[0046] Namely, in the article having a metal oxide coating 1 disclosed herein, since the metal oxide particles that compose the metal oxide coating 3 have a minute size as previously described, they typically have high crystallinity and are both colorless and transparent with respect to visible light. Thus, the metal oxide coating 3 having the above-mentioned structure also has high transmittance with respect to visible light and can be transparent (including being colorless and transparent) in the same manner as the inherent properties of the metal oxide particles. With respect to this point, the article having a metal oxide coating 1 is provided with metallic luster attributable to the metal material of the base material 2 despite being coated with metal oxide particles.

[0047] On the other hand, the metal oxide that composes the metal oxide particles is provided with a prescribed refractive index based on the composition thereof. Thus, a difference in the optical path results between light that has been radiated onto the article having a metal oxide coating 1 and reflected by the surface of the article having a metal oxide coating 1, and light that has passed through the metal oxide coating 3 and been reflected by the surface of the base material 2. When this optical path difference becomes an integral multiple of the wavelength of light of a prescribed color, light of that wavelength is intensified by an interference phenomenon of light, thereby making it appear as if the article having a metal oxide coating I has been colored to the color based on that wavelength. This optical path difference changes according to the refractive index of the metal oxide that composes the metal oxide coating 3, the thickness of the metal oxide coating 3 and the angle at which the article having a metal oxide coating 1 is viewed. Thus, the article having a metal oxide coating 1 is able to realize various tints accompanied by brightness based on this optical path difference. In addition, the tint can be given variability depending on the angle at which the article having a metal oxide coating 1 is viewed.

[0048] Furthermore, as shown in Fig. 1, in the article having a metal oxide coating 1, the interface between the base material 2 and the metal oxide coating 3 as well as the surface of the metal oxide coating 3 are not completely smooth. In addition, interfaces and minute gaps can be formed between the metal oxide particles that compose the metal oxide coating 3 and between the metal oxide particles and the base material 2. Thus, the above-mentioned optical effects can be changed even more diversely due to disruption of orderliness by this complex and minute interface structure. As a result, for example, metallic luster attributable to the base material 2 is diminished, and the gloss accompanied by color as described above is able to demonstrate a softer brightness. In addition, in the case of viewing the article having a metal oxide coating 1 from a prescribed angle, instead of being limited to emphasis of light of a specific wavelength, light of various wavelengths, for example, is mixed, and the article having a metal oxide coating 1 is able to demonstrate a white color tinted with brightness (milky white color).

[Production of Article having Metal Oxide Coating]

[0049] The article having a metal oxide coating 1 disclosed herein can be preferably produced according to, for example, the method indicated below. Namely, in the method for producing the article having a metal oxide coating 1, metal oxide particles can be immobilized directly on the base material 2 by supplying metal oxide particles to the surface of the base material 2 and adhering the metal oxide particles to the base material 2. Thus, a preferable method for producing the article having a metal oxide coating 1 disclosed herein includes, for example, a step for forming the metal oxide coating 3 by polishing the surface of the base material 2 using the metal oxide particles.

[Preparation of Base Material]

[0050] Various types of base materials composed of the previously described metal materials can be used for the base material 2. The base material 2 is preferably provided with a flat surface on at least a portion of the surface thereof. This flat surface may be provided by polishing the surface of the base material 2 prior to forming the metal oxide coating 3. Mirrored surface polishing using a polishing slurry selected corresponding to the material of the base material 2 can be used for this polishing. Although there are no particular limitations thereon, this polishing can typically be preferably realized by, for example, chemical mechanical polishing (CMP) using a polishing slurry containing colloidal silica as loose abrasive. A detailed explanation of technology relating to this mirrored surface polishing is omitted here since it is unrelated to the present invention.

[Formation of Metal Oxide Coating]

[0051] Next, polishing is carried out on the base material 2 prepared in the manner described above using a liquid composition containing the metal oxide particles for the polishing slurry. This polishing can be preferably carried out using, for example, CMP technology. Namely, during polishing using a liquid composition containing the metal oxide particles for the polishing slurry, in addition to the surface chemical effects of the metal oxide particles per se, the effects of chemical components contained in the polishing slurry on the surface of the base material 2 can also be utilized. As a result, the metal oxide coating 3 is formed due to the surface of the base material 2 being transformed to a state that is suitable for immobilizing the metal oxide particles, and dense and uniform adhesion and immobilization of metal oxide particles being realized on the base material 2.

[0052] Furthermore, there are no particular limitations on the polishing machine used for this polishing, and for example, various types of commercially available polishing machines can be used. More specifically, a so-called stationary or portable polishing machine, or a polishing machine for metal processing or precision polishing, for example, can be used.

[0053] Here, the metal oxide particles contained in the liquid composition used for polishing may be in the form of primary particles or in the form of secondary particles formed by aggregation of a plurality of primary particles. In addition, the metal oxide particles may include a mixture of metal oxide particles in the form of primary particles and metal oxide particles in the form of secondary particles. In a preferred aspect thereof, at least a portion of the metal oxide particles are contained in the liquid composition in the form of secondary particles. The mean primary particle diameter of metal oxide particles contained in the liquid composition is within a range that allows the realization of the mean primary particle diameter of the metal oxide particles that compose the metal oxide coating 3. Namely, the mean primary particle diameter is roughly equal to the mean primary particle diameter of the metal oxide particles that compose the metal oxide coating 3.

[0054] In addition, although there are no particular limitations thereon, the mean secondary particle diameter of the metal oxide particles is preferably made to be about 10 nm to 10 μm. From the viewpoint of, for example, the efficiency at which the metal oxide particles are immobilized on the base material 2, the mean secondary particle diameter of the metal oxide particles is preferably 50 nm or more and more preferably 100 nm or more. In addition, from the viewpoint of being able to form the metal oxide coating 3 having a more uniform thickness, the mean secondary particle diameter of the abrasive is suitably 2 μm or less, preferably 1.5 μm or less and more preferably 1 μm or less.

[0055] Furthermore, the cumulative 50% particle diameter (D_{50}) based on volume-based particle size distribution as measured using a commercially available particle size analyzer can be used for the mean secondary particle diameter of the metal oxide particles. An analyzer based on any of the methods of dynamic laser scattering, laser diffraction, laser scattering or pore electrical resistance method can be used for the particle size distribution analyzer.

[0056] In addition, the mean primary particle diameter of the metal oxide particles contained in the liquid composition can be measured by observing with an electron microscope in the same manner as the mean primary particle diameter of the metal oxide particles composing the metal oxide coating 3 as previously described.

[0057] In addition, there are no particular limitations on the liquid medium of the liquid composition in which the metal oxide particles are dispersed. For example, a liquid medium similar to the liquid medium of a conventional polishing slurry used for CMP can be used as a preferable example of a liquid medium. This liquid medium is typically composed mainly of water, and can contain a dispersant or surfactant that enhances dispersibility of the metal oxide particles, and further contain a pH adjuster and the like as necessary. The liquid composition can contain various types of additives used in this type of field within a range that does not greatly impair production of the article having a metal oxide coating 1. Furthermore, although varying according to the material of the base material 2, the pH of the liquid composition is expected to be able to have an effect on the mode of adhesion of the metal oxide particles to the base material 2. In a preferred aspect, the pH of the liquid composition is preferably adjusted to, for example, the alkaline side (pH in excess of 7, typically pH 8 to pH 13, and for example, about pH 9 to pH 11).

[0058] The polishing composition of the present invention may further contain, as necessary, other components such as an etching agent that promotes dissolution of alloy materials, an oxidizing agent that oxidizes the surface of alloy materials, a water-soluble polymer, copolymer or salt or derivative thereof that acts on the surfaces of alloy materials and abrasives, an anticorrosive or chelating agent that inhibits corrosion of the surface of alloy materials, a dispersion assistant that facilitates re-dispersion of aggregates of abrasive, or a preservative or anti-mold agent having other functions.

[0059] Examples of etching agents include inorganic acids such as nitric acid, sulfuric acid or phosphoric acid, organic acids such as acetic acid, citric acid, tartaric acid or methanesulfonic acid, inorganic bases such as potassium hydroxide or sodium hydroxide, and organic bases such as ammonia, amines or quaternary ammonium hydroxides.

[0060] Examples of oxidizing agents include hydrogen peroxide, peracetic acid, percarbonates, urea peroxide, perchlorates and persulfates.

[0061] Examples of water-soluble polymers, copolymers or salts or derivatives thereof include polycarboxylic acids such as polyacrylates, polysulfonic acids such as polysulfonic acid or polystyrene sulfonic acid, polysaccharides such as xanthan gum or sodium alginate, cellulose derivatives such as hydroxyethyl cellulose or carboxymethyl cellulose, polyethylene glycol, polyvinyl alcohol, polyvinylpyrrolidone, polyoxyethylene alkyl ether, polyoxyethylene alkyl phenyl ether, sorbitan monooleate and oxyalkylene-based polymers having a single type or plurality of types of oxyalkylene units.

[0062] Examples of anticorrosive agents include amines, pyridines, tetraphenyl phosphonium salts, benzotriazoles, triazoles, tetrazoles and benzoic acid.

[0063] Examples of chelating agents include carboxylic acid-based chelating agents such as gluconic acid, amine-based chelating agents such as ethylenediamine, diethylenetriamine or trimethyltetramine, polyaminopolycarboxylic acid-based chelating agents such as ethylenediamine tetraacetic acid, nitrilotriacetic acid, hydroxyethyl ethylenediamine triacetic acid, triethylenetetramine hexaacetic acid or diethylenetriamine pentaacetic acid, organic phosphonic acid-based chelating agents such as 2-aminoethylphosphonic acid, 1-hydroxyethylidene-1,1-diphosphonic acid, aminotri(methylene phosphonic acid), ethylenediamine tetraquis(methylene phosphonic acid), diethylenetriamine penta(methylene phosphonic acid), ethane-1,1-diphosphonic acid, ethane-1,1,2-triphosphonic acid, methanehydroxyphosphonic acid or 1-phosphobutane-2,3,4-tricarboxylic acid, phenol derivatives and 1,3-dietones.

[0064] Examples of dispersion assistants include condensed phosphates such as pyrophosphates or hexametaphosphates. Examples of preservatives include sodium hypochlorite. Examples of anti-mold agents include oxazolines such as oxazolidine-2,5-dione.

[0065] Next, the liquid composition is supplied as polishing slurry to the polishing target in the form of the base material 2 followed by polishing according to an ordinary method. During polishing, for example, the base material 2 is immobilized on an ordinary polishing device and polishing slurry is supplied to the surface of the base material 2 (polishing target surface) through a polishing pad of the polishing device. Typically, the polishing pad is contacted with the surface of the base material 2 and both are moved relative to each other (such as by rotational movement) while continuously supplying the polishing slurry. According to this polishing step, metal oxide particles are adhered and immobilized on the surface of the base material 2 and formation of the metal oxide coating 3 is completed. The article having a metal oxide coating I disclosed herein is produced as a result thereof.

[0066] Furthermore, there are no particular limitations on the polishing pad used in the polishing step. For example, a nonwoven fabric type or suede type of polishing pad, or a polishing pad containing an abrasive or not containing an abrasive, may be used.

[0067] In addition, the article having a metal oxide coating 1 produced in the manner described above is typically subjected cleaning after polishing. This cleaning can be carried out using a suitable cleaning solution.

[Application]

[0068] The article having a metal oxide coating 1 disclosed herein is provided in the form of an article in which color and luster have been imparted to the surface of a metal material of various materials and shapes, and is provided with high designability. Thus, it can be preferably applied to constituent members composing various types of products, and particularly members requiring high designability and esthetics. Members of various types of articles used in commercial applications can typically be considered for such members, and for example, these can be articles requiring diverse designability supplied to ordinary users. More specifically, these articles can be preferably used as articles represented by, for example, household goods such as various types of electrical products, kitchenware, interior articles or exterior articles, building materials such as window frames or door materials, and interior and exterior materials used in automobiles, bicycles, motorcycles and the like.

[0069] In addition, in another aspect, the article having a metal oxide coating 1 disclosed herein is provided with a metal oxide coating 3 composed of a metal oxide on the surface thereof. Thus, the surface of the base material 2 can be imparted with various functions according to the metal oxide that composes the metal oxide coating. Examples of such functions include one or more functions among corrosion resistance, heat resistance, abrasion resistance and chemical stability and the like. Moreover, the article having a metal oxide coating 1 disclosed herein can be made to have lower glossiness in comparison with a mirrored surface. From this viewpoint, the article having a metal oxide coating 1 can be preferably used in optical article applications requiring control (and typically, inhibition) of light reflection properties.

[0070] Although the following provides an explanation of several examples relating to the present invention, the present invention is not intended to be limited by that indicated in the examples.

(Examples I to 12)

[0071] Commercially available plates composed of three types of aluminum alloys formed of "Al1070", "Al5052" and "Al6063" were prepared and cut out to dimensions of 32 mm × 32 mm to obtain Base Materials 1 to 3 in that order. Furthermore, the last four digits of these base materials indicate the alloy numbers of the aluminum alloy plates as defined in JIS H4000:2006, and each base material has a composition corresponding to that alloy number. In addition, the Brinell hardness (10/500) of Base Materials 1 to 3 is 26-75 for Base Material 1, 60-77 for Base Material 2 and 60 for Base Material 3.

[0072] These base materials were placed on the carrier of a polishing machine and initially subjected to mirrored surface polishing so that the surface roughness Ra was about 5 nm.

[0073] Next, the surface of the base materials subjected to mirrored surface polishing was polished using liquid compositions containing the metal oxide particles indicated in the following Examples 1 to 12 as polishing slurrys. Furthermore, the polishing conditions used during polishing are as indicated below.

<Examples 1 to 3>

[0074] A liquid composition containing zirconium oxide particles having a mean secondary particle diameter of 0.9 μm at a content ratio of 200 g/L was prepared and used as polishing slurry.

[0075] Furthermore, the pH of the liquid composition of Example 1 was adjusted to 3.0 with citric acid.

[0076] The pH of the liquid composition of Example 2 was 6.0.

[0077] The pH of the liquid composition of Example 3 was adjusted to 10.0 with potassium hydroxide.

<Examples 4 to 6>

[0078] A liquid composition containing cerium oxide particles having a mean secondary particle diameter of 1.4 μm at a content ratio of 200 g/L was prepared and used as polishing slurry.

[0079] Furthermore, the pH of the liquid composition of Example 4 was adjusted to 3.0 with citric acid.

[0080] The pH of the liquid composition of Examples 5 was 6.7.
[0081] The pH of the liquid composition of Example 6 was adjusted to 10.0 with potassium hydroxide.

<Examples 7 to 9>

[0082] A liquid composition containing aluminum oxide particles having a mean secondary particle diameter of 1.2 μm at a content ratio of 200 g/L was prepared and used as polishing slurry.
[0083] Furthermore, the pH of the liquid composition of Example 7 was adjusted to 3.0 with citric acid.
[0084] The pH of the liquid composition of Example 8 was 7.1.
[0085] The pH of the liquid composition of Example 9 was adjusted to 10.0 with potassium hydroxide.

<Examples 10 to 11>

[0086] A liquid composition containing colloidal silica having a mean secondary particle diameter of 60 nm at a content ratio of 18% by mass was prepared and used as polishing slurry.
[0087] Furthermore, the pH of the liquid composition of Example 10 was adjusted to 4.0 with citric acid.
[0088] The pH of the liquid composition of Example 11 was adjusted to 7.0 with potassium hydroxide.
[0089] The pH of the liquid composition of Example 12 was adjusted to 10.0 with potassium hydroxide.

[Polishing Conditions]

[0090]

Polishing machine: Single side polishing machine (Polishing plate diameter: 380 mm)
Polishing pad: Suede type
Polishing pressure: 175 g/cm^2
Plate rotating speed: 90 rpm
Linear velocity; 72 m/min
Polishing time: 10 min
Polishing slurry temperature: 20°C
Flow rate of Polishing slurry: 14 ml/min

[0091] Furthermore, the types of metal oxide particles contained in the liquid compositions of Examples 1 to 12 and the pH of the liquid compositions are shown in the following Table 1. Polishing with the liquid compositions of Examples 1 to 3 was carried out by simultaneously placing Base Materials 1 to 3 on the carrier of the polishing machine and polishing under the same conditions.
[0092] Values for mean secondary particle diameter of the metal oxide particles contained in the liquid compositions of Examples 1 to 9 were measured by laser diffraction/scattering particle size distribution analysis using a particle size analyzer (Model LA-950, Horiba, Ltd.).
[0093] Values for mean secondary particle diameter of aggregated particles of colloidal silica contained in the liquid compositions of Examples 10 to 12 were measured by dynamic light scattering using a particle size analyzer (Model UPA-UT151, Nikkiso Co., Ltd.).
[0094] The polished surfaces of base materials obtained by polishing with the liquid compositions of Examples 1 to 12 (to also simply be referred to in the manner of the "Base Material of Example 1") were measured for color tone, glossiness, degree of coloration and polished surface roughness as indicated below, and those results are shown in Table 1. Furthermore, each evaluation was carried out under the conditions indicated below.

<Color Tone>

[0095] The color tone of the polished surface of the base material after polishing was evaluated visually. Evaluation criteria included classifying the color tone of the base material as any of red, orange, yellow, green, blue, violet, white, black or no change based on the metallic luster of the surface of the base material after polishing. The results are shown in the "Color tone" column of the following Table 1. Furthermore, a "-" mark in the table indicates the case in which the color tone of the surface had not undergone any particular change (no change).

<Degree of Coloring>

[0096] The degree of coloring of the polished surface of the base material after polishing was evaluated visually on a scale from 0 to 5. The evaluation criteria were such that a higher value indicates deeper coloring, with a degree of coloring of 0 indicating a metallic luster that is not colored (namely, equivalent to the metallic luster of the mirror polished surface). The results are shown in the "Degree of coloring" column of the following Table 1.

<Glossiness>

[0097] Glossiness of the polished surface of the base material after polishing was measured at a measuring angle of 20° using the "GM-268Plus" gloss meter manufactured by Konica Minolta Optics, Inc. based on the methods used to measure specular glossiness described in JIS Z8741:1997. The results are shown in the "Glossiness" column of the following Table 1.

<Surface Roughness>

[0098] Surface roughness Ra of the polished surface of the base material after polishing was measured over a measurement field of 1.4 mm × 1.1 mm using a non-contact surface profile measuring instrument (NewView 5032, Zygo Corporation.). The results are shown in the "Ra" column of the following Table 1.
[0099] [Table 1]

Table 1

Example	Base material	Metal oxide particles	Polishing slurry pH	Color tone	Degree of coloring	Glossiness	Ra (nm)
1	3	Zirconium oxide	3.0	White	1	961	1.8
	2			White	1	1089	2.3
	1			White	1	747	1.2
2	3	Zirconium oxide	6.0	White	2	798	7.2
	2			White	2	962	6
	1			White	2	495	2.1
3	3	Zirconium Oxide	10.0	Yellow	5	170	3.5
	2			Yellow	5	319	5
	1			Red	5	30	27
4	3	Cerium oxide	3.0	White	3	353	8.5
5			6.7	White	3	205	12.3
6			10.0	White	4	114	11.5
7	3	Aluminum oxide	3.0	White	2	608	3.7
8			7.1	White	4	109	15.3
9			10.0	White	3	200	6.1
10	3	Colloidal silica	4.0	-	0	1827	1.6
11			7.0	-	0	1829	1.8
12			10.0	-	0	1848	1.8

[0100] As shown in Table 1, the surfaces of the base materials of Examples 1 to 9 were confirmed to demonstrate color ranging from white to yellow and red while maintaining metallic luster. As a result, high designability provided with unique color and luster was confirmed to be imparted to the base materials of Examples I to 9. In contrast, although the surfaces of the base materials of Examples 10 to 12 maintained metallic luster, coloring of those surfaces was unable to be confirmed. Furthermore, glossiness was low for the colored base materials of Examples 1 to 9, while extremely high values were confirmed for the glossiness of the base materials of Examples 10 to 12. In addition, although unable to be determined unequivocally as a result of being evaluated by sensory evaluations, glossiness generally tended to be lower the higher the degree of coloring.
[0101] On the basis of the above, the color imparted to the base materials of Examples 1 to 9 was expected to be

attributable to the various types of metal oxide particles contained in the liquid compositions used as polishing slurry being adhered to and immobilized on the base materials. In addition, the reason for the base materials of Examples 10 to 12 not demonstrating color is expected to be due to the use of colloidal silica for the metal oxide particles contained in the liquid compositions used as polishing slurry, and the difficulty in adhering the colloidal silica to the base materials under the polishing conditions used in the examples due to the nearly spherical shape thereof.

[0102] Furthermore, although specific results are not shown, as a result of observing the surface of Base Material 3 of Example 3 after polishing with a transmission electron microscope, the colored surface of Base Material 3 of Example 3 was confirmed to be densely coated with particles having a diameter of about 50 nm to 100 nm. When a cross-section of Base Material 3 was observed after polishing, these particles were able to be confirmed to be adhered to the surface of Base Material 3 in the form of a film formed of one or two or more layers that appeared to be anchored therein. In addition, these particles were able to be confirmed to adhere to the surface of Base Material 3 in a coherent state in the form of a film having a thickness of about 100 nm. These particles were determined to have dimensions and shape that roughly coincide with those of the primary particles of zirconium oxide contained in the polishing slurry. In addition, the surface roughness Ra of Base Material 3 of Example 3 is presumed to be attributable to the arrangement of the particles.

[0103] Moreover, based on the results of a compositional analysis of a cross-section of Base Material 3 of Example 3 by EDX, the particles were able to be confirmed to be metal oxide (zirconium oxide) particles contained in the liquid composition used as polishing slurry. In addition, the size and shape of the particles adhered to the base material were able to be confirmed to closely coincide with the size and shape of primary particles composing zirconium oxide particles, and the shape of the zirconium oxide particles was able to be confirmed to not have undergone any significant deformation. These zirconium oxide particles were also confirmed to be present on the surface of the base material so as to form a film having a thickness corresponding to the dimensions thereof (such as primary particle diameter). As a result, an article having a metal oxide coating was able to be confirmed to be formed by polishing Base Material 3 using the liquid composition of Example 3.

[0104] On the basis of the above results, the surfaces of the base materials of Examples 1 to 9 having colored surfaces are also presumed to have formed articles having a metal oxide coating as a result of metal oxide particles adhering in the same manner as the surface of Base Material 3 of Example 3. In addition, based on the surface roughness Ra of each of these base materials, surface roughness Ra is presumed to have been realized as a result of each of the metal oxide particles being adhered to and arranged on the base material in the form of primary particles. On the other hand, the base materials of uncolored Examples 10 to 12 are presumed to not be coated with particles in this manner based on such factors as the glossiness thereof.

[0105] Furthermore, the reason for the base material of Example 3 being colored yellow to red while the base materials of Examples 1, 2 and 4 to 9 were colored white was thought to be due to the structure of the metal oxide coating formed by metal oxide particles adhered to each base material and the effects of light. Namely, the optical path difference of the metal oxide coating composed of metal oxide particles adhered to the base material of Example 3, which is determined by, for example, the refractive index and thickness thereof (which can be the density of the metal oxide particles and distribution thereof), is thought to coincide with conditions enabling interference of light having a wavelength corresponding to yellow and/or red color.

[0106] On the other hand, optical interference is known to be perceived as white color when the optical path difference matches the following conditions: (1) optical path difference is shorter than the wavelength of visible light, and (2) optical path difference nearly matches strongly overlapping wavelengths. With respect to the base materials of the other Examples 1,2 and 4 to 9, the status of the interface between the base material and metal oxide coating or the structure of the metal oxide coating is equivalent to the conditions of (1) or (2) described above, and these base materials demonstrated white color as a result thereof.

[0107] On the basis of the above, a metal material was able to be confirmed to be able to demonstrate color by directly adhering metal oxide particles to the surface of a base material composed of that metal material by polishing and the like.

[0108] Furthermore, in the examples described here, aluminum alloy was used for the base material since it has high reflectance and facilitates distinction of differences between each example as described above. However, on the basis of the above results, it can be understood by a person with ordinary skill in the art that effects similar to those described above can also be obtained in the case the base material is a metal material other than aluminum alloy provided that metal oxide particles are adhered to the surface thereof.

[0109] Although specific examples of the present invention have been described in detail above, these are merely for illustrations and do not limit the scope of the claims. The technology described in the claims includes various modifications and changes made to the specific examples illustrated above. Reference Signs List

[0110]

1 Article having metal oxide coating
2 Base material
3 Metal oxide coating

Claims

1. An article having a metal oxide coating, the article comprising:

a base material comprising a metal material; and
a metal oxide coating comprising a metal oxide coated onto a surface of the base material, the metal oxide coating being formed by polishing the surface of the base material, using particles composed of the metal oxide.

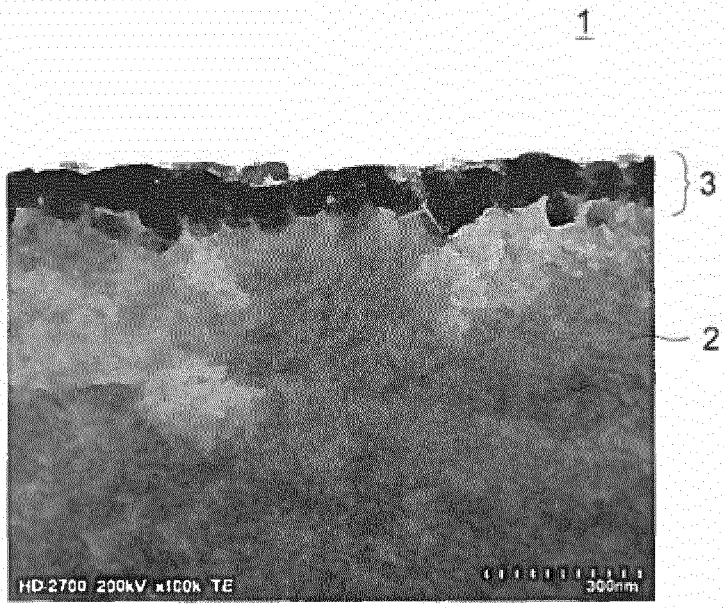
2. The article having a metal oxide coating according to claim 1, wherein a mean primary particle diameter of the particles comprising the metal oxide is 10 nm to I μm.

3. The article having a metal oxide coating according to claim 1 or 2, wherein the base material comprises a metal material having a Brinell hardness of 10 to 200.

4. The article having a metal oxide coating according to any of claims 1 to 3, wherein the metal oxide particles comprise one or more types of oxides selected from the group consisting of zirconium oxide, cerium oxide and aluminum oxide.

5. The article having a metal oxide coating according to any of claims 1 to 4, wherein the base material comprises aluminum or aluminum alloy.

[Fig. 1]



INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2014/082099

A. CLASSIFICATION OF SUBJECT MATTER
B32B15/16(2006.01)i, *B24B1/00*(2006.01)i, *B24B37/00*(2012.01)i, *B32B9/00*(2006.01)i, *C23C24/06*(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)
B32B15/16, B24B1/00, B24B37/00, B32B9/00, C23C24/06

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	1996-2014
Kokai Jitsuyo Shinan Koho	1971-2014	Toroku Jitsuyo Shinan Koho	1994-2014

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.
X	JP 2000-34669 A (Nissan Chemical Industries, Ltd.), 02 February 2000 (02.02.2000), paragraphs [0001], [0022], [0045], [0060] to [0061] (Family: none)	1-5
A	JP 62-99071 A (Kobe Steel, Ltd.), 08 May 1987 (08.05.1987), page 2, lower right column, line 4 to page 3, upper right column, line 6; tables 1 to 2 (Family: none)	1-5
A	JP 10-121034 A (Showa Denko Kabushiki Kaisha), 12 May 1998 (12.05.1998), paragraphs [0010] to [0022] & US 5935278 A	1-5

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

* Special categories of cited documents:
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"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	Date of mailing of the international search report
18 December 2014 (18.12.14)	06 January 2015 (06.01.15)

Name and mailing address of the ISA/	Authorized officer
Japan Patent Office	
Facsimile No.	Telephone No.

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

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2014/082099

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 61-291674 A (Kobe Steel, Ltd.), 22 December 1986 (22.12.1986), page 1, lower left column, line 16 to page 2, upper left column, line 12 (Family: none)	1-5
A	JP 2013-158860 A (Hitachi Chemical Co., Ltd.), 19 August 2013 (19.08.2013), paragraphs [0024] to [0054] (Family: none)	1-5

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

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- JP 2013258722 A **[0001]**
- JP H2185365 B **[0003]**
- JP H4201069 B **[0003]**
- JP H7256555 B **[0003]**
- JP H10036819 B **[0003]**