

SPECIFICATION

Title of the Invention: Water-Reactive Al Composite Materials, Water-Reactive Al Alloy-Sprayed Films, Methods for Preparing the Al Alloy-Sprayed Films, and Constituent members for Film Deposition Chambers

Technical Field

[0001]

The present invention relates to a water-reactive Al composite material, a water-reactive Al alloy-sprayed film, a method for the preparation of the Al alloy-sprayed film, and constituent members for a film deposition chamber and, in particular, to a water-reactive Al composite material comprising Al to which Bi, Si, Ti, Ce and Mg are added; a water-reactive Al alloy-sprayed film consisting of this water-reactive Al composite material; a method for the preparation of the Al alloy-sprayed film; and a component covered with the Al alloy-sprayed film and used in a film deposition chamber.

Background Art

[0002]

In a film deposition apparatus used for forming a thin film according to a method such as the sputtering technique, the vacuum deposition technique, the ion plating technique, the CVD technique or the like, constituent members used in the film deposition chamber of such an apparatus, which are arranged within the same, are inevitably covered with a metal or metal compound film consisting of film deposition materials and deposited thereon during the film deposition process. As such constituent members for the film deposition chamber, there may be listed, for example, an adhesion

preventive film for preventing the adhesion of a film on the inner part of a vacuum chamber other than a substrate; a shutter; a mask for forming a film only on the desired portions on the substrate; a tray for transporting a substrate, or the like. During the film deposition process, a film having a composition identical to that of an intended thin film (a thin film to be deposited on the substrate) is also adhered to these constituent members. It is common that these constituent members are repeatedly used after the removal or peeling of the film adhered thereto.

[0003]

A film inevitably adhered to these constituent members for a film deposition chamber would have a thickness which is increased in proportion to the operating time of a film deposition process. Such an adhered film would be released or peeled off from the constituent members for the film deposition chamber in the form of particles due to the action of the internal stress thereof and the stress attributable to repeated thermal history, the particles are in turn adhered onto a substrate to be processed and this becomes a cause of film defects. For this reason, constituent members for a film deposition chamber are periodically subjected to the following processing cycle: the removal of the constituent members from a film deposition apparatus at the stage in which a film adhered to these members is not yet peeled off from the same during the film-forming operation; the washing of the constituent members to remove the film deposited thereon; the subsequent surface finishing of the constituent members; and the reuse thereof.

[0004]

When using, for example, valuable metals such as Al, Mo, Ti, Cu, Ag, Au, Pt, Rh, Ru, Ir, Ta, W, Nb, Zr, Re, Ni, Cr, V, Li, Co, Pd, Nd, In and Se; alloys consisting of at least two of such valuable metals; and oxides such as ITO, ZnO, PZT and TiO₂, as film deposition materials, there has been desired for the establishment of an inexpensive processing technique which may permit the recovery of, for example, a metal adhered to a component other than a substrate without taking part in the formation of a film on the substrate and which may likewise permit the recycle of the component.

[0005]

For instance, in the case of an adhesion preventive plate, used in a film deposition apparatus, for preventing the adhesion of film deposition materials on the inner walls of the apparatus other than a substrate as well as the surface of each constituent member for a film deposition chamber, the plate is, under the present conditions, reused after the peeling off of the deposits formed thereon during the film deposition process. Examples of methods for removing such deposits, generally used, include the sand-blasting technique; the wet etching technique using an acid or an alkali; the peeling method which makes use of the hydrogen embrittlement caused by the action of, for instance, hydrogen peroxide, as well as the peeling method with the use of the electrolytic technique. In this case, the adhesion preventive plate or the like likewise receives not a little damage when carrying out the treatment for peeling off of the deposits and therefore, there is a limit on the number of the reuse times thereof. For this reason, there

has been a need for the development of any technique for reducing the damages of the adhesion preventive plate or the like as low as possible.

[0006]

5 In addition to the adhesive film-peeling methods as discussed above, a technique has been known, which comprises the steps of carrying out a film deposition process in an apparatus equipped with constituent members each covered with an Al alloy-sprayed film consisting of a water-reactive
10 Al composite material which has such a property that it can undergo a reaction in a moisture-containing atmosphere to thus make the same soluble therein; removing and separating the film adhered to the constituent members during the film deposition process through such a reaction and dissolution
15 of the Al alloy-sprayed film; and recovering the valuable metals included in the film deposition materials from the adhered film thus removed or peeled off from the constituent members. As such water-reactive Al composite materials, there may be mentioned, for instance, those comprising Al to
20 which In, Si and Ti are added in certain amounts (see, for instance, Patent Document 1 listed below); and those comprising Al to which Bi and Si are added in certain amounts (see, for instance, Patent Document 2 listed below). However, these materials cannot necessarily be satisfied for the
25 reasons, for instance, that it takes a long period of time to remove the Al alloy-sprayed film which has been subjected to a film deposition process at a high temperature and that the strength of the Al alloy-sprayed film derived from the same is low.

30 **List of Prior Art**

Patent Documents:

[0007]

Patent Document 1: Patent Official Gazette No. 5,517,371

Patent Document 2: Patent Official Gazette No. 5,327,759

5 Disclosure of the Invention

Problems That the Invention is to Solve:

[0008]

It is a subject of the present invention to solve the problems associated with the aforementioned prior arts and more particularly to provide a water-reactive Al composite material for thermal spraying, which comprises Al in combination with Bi, Si, Ti, Ce and Mg incorporated therein and which can form a film capable of undergoing a reaction within a moisture-containing atmosphere to thereby make the film soluble therein; an Al alloy-sprayed film consisting of the Al composite material; a method for the preparation of the Al alloy-sprayed film; and a constituent member for a film deposition chamber, which is covered with the Al alloy-sprayed film.

20 Means for Solving the Problems

[0009]

The water-reactive Al composite material for use in a thermal spraying process, according to the present invention, is characterized in that it comprises Al to which are added, on the basis of the weight of the Al, Bi in an amount of not less than 0.2% by mass and not more than 2% by mass, preferably not less than 0.5% by mass and not more than 1.5% by mass; Si in an amount of not less than 1.5% by mass and not more than 8% by mass, preferably not less than 3% by mass and not more than 5% by mass; Ti in an amount of not

less than 0.2% by mass and not more than 4% by mass, preferably not less than 1% by mass and not more than 2% by mass; Ce in an amount of not less than 0.2% by mass and not more than 2% by mass, preferably not less than 0.2% by mass and not more than 0.5% by mass; and Mg in an amount of not less than 0.2% by mass and not more than 2% by mass, preferably not less than 0.5% by mass and not more than 2% by mass.

[0010]

10 If the water-reactive Al composite material for thermal spraying has such a composition specified above, the Al film formed from the material can easily undergo a reaction with water within a moisture-containing atmosphere so that the Al film can be dissolved therein while generating hydrogen gas.

15 [0011]

 If the amount of Bi is less than 0.2% by mass, the resulting Al composite material has such a tendency that the reactivity thereof with water is reduced, while if the amount thereof is not less than 0.2% by mass and less than 0.5% by mass, the resulting Al composite material shows such a tendency that the reactivity thereof with water is slightly low, but if it is not less than 0.5% by mass, the resulting composite material shows a tendency that the composite material is satisfied with its reactivity with water and if it is higher than 2% by mass, the resulting composite material shows such a tendency that the reactivity thereof with water is quite high and would thus undergo a reaction even with the moisture within the atmospheric air. If the amount of Si is less than 0.7% by mass, there is observed a tendency that the resulting composite material has a reduced

effect of controlling the reactivity with water, while if it exceeds 5% by mass, when melting the Al composite material to form an ingot and then processing the ingot composed of the composite material to thus give a wire, there is observed
5 such a tendency that the drawing of an ingot into a wire becomes difficult, while if it exceeds 8% by mass, the ingot of the Al composite material shows a tendency that the material cannot be processed into a wire having a diameter reduced to a level of 3.1mm ϕ (the recommended size of a
10 spraying gun as will be described later). If the amount of Ti is less than 0.2% by mass, the resulting Al alloy-sprayed film, which has gone through thermal history during a film deposition process, shows a tendency to have a reduced solubility. In this respect, there is observed such a
15 tendency that the higher the added amount of Ti, the better the solubility of the Al alloy-sprayed film after going through thermal history. However, when processing an ingot of the molten composite material in the form of a wire, there is such a tendency that it becomes difficult to draw the
20 ingot (the molten composite material) into a wire when the amount of Ti is about 4% by mass or higher. If the Al composite material is free of Ce, the resulting Al alloy-sprayed film after going through thermal history is apt to be reduced in its solubility, while if it exceeds 0.5% by
25 mass, any exceptional improvement in the solubility cannot be attained any more. If the Al composite material is free of Mg, the resulting Al alloy-sprayed film after going through thermal history has a reduced stability, undergoes a reaction with the moisture within the atmospheric air and
30 causes a powdering (or chalking) phenomenon. If the amount

of Mg is less than 0.2% by mass, a powdering phenomenon is observed, in a slight degree, on the surface of the resulting Al alloy-sprayed film after it goes through thermal history, while if it is not less than 0.5% by mass, any powdering phenomenon is not observed. When processing the molten composite material into an ingot, there is observed such a tendency that the drawing of the ingot into a wire becomes difficult when the amount of Mg is about 2% by mass or higher. [0012]

10 The method for preparing a water-reactive Al alloy-sprayed film according to the present invention is characterized in that it comprises the steps of melting a material comprising Al to which are added, on the basis of the weight of the Al, Bi in an amount of not less than 0.2% by mass and not more than 2% by mass, preferably not less than 0.5% by mass and not more than 1.5% by mass; Si in an amount of not less than 1.5% by mass and not more than 8% by mass, preferably not less than 3% by mass and not more than 5% by mass; Ti in an amount of not less than 0.2% by mass and not more than 4% by mass, preferably not less than 1% by mass and not more than 2% by mass; Ce in an amount of not less than 0.2% by mass and not more than 2% by mass, preferably not less than 0.2% by mass and not more than 0.5% by mass; and Mg in an amount of not less than 0.2% by mass and not more than 2% by mass, preferably not less than 0.5% by mass and not more than 2% by mass, in such a manner that the composition of the resulting material becomes uniform; thermally spraying the resulting molten material on the surface of a base material; and then quenching and solidifying the molten material sprayed on the base material

to thus form a film thereon.

[0013]

The water-reactive Al alloy-sprayed film according to the present invention is characterized in that it consists
5 of the foregoing water-reactive Al composite material for thermal spraying.

[0014]

The constituent members for the film deposition chamber of a film deposition apparatus, according to the present
10 invention, are characterized in that each of them is provided with the aforementioned water-reactive Al alloy-sprayed film on the surface thereof.

[0015]

The foregoing constituent member is preferably an
15 adhesion preventive plate, a shutter or a mask.

Effects of the Invention

[0016]

The Al alloy-sprayed film, which consists of the water-reactive Al composite material for thermal spraying,
20 according to the present invention, would have the following effects: the Al alloy-sprayed film can easily be prepared using a simple process at low cost; in addition, it has such a characteristic feature that it can react with water in a moisture-containing atmosphere and can be dissolved therein
25 even after going through thermal history attributable to the film deposition process at a high temperature (for instance, about 350°C); and at the same time, the degree of activity thereof prior to experiencing such thermal history (on and after the film deposition) can be controlled, by the addition
30 of every metals discussed above in desired amounts.

[0017]

The water-reactive Al alloy-sprayed film according to the present invention can undergo a reaction in the presence of moisture and be effectively dissolved therein while generating hydrogen. Therefore, the Al alloy-sprayed film likewise shows such effects that if a film is formed using a film deposition apparatus equipped with constituent members (such as an adhesion preventive plate, a shutter, a mask and the like) for a film deposition chamber, which are covered with this water-reactive Al alloy-sprayed film, inevitably adhered films, which consist of film deposition materials and would be adhered to the surface of, for instance, an adhesion preventive plate during the film deposition process, can be peeled off and separated from the constituent members through the reaction and dissolution of the Al alloy-sprayed film and that valuable metals present in the film deposition materials can easily be recovered from the adhered films thus peeled off.

[0018]

Moreover, the covering of constituent members for a film deposition chamber with the water-reactive Al alloy-sprayed film according to the present invention would permit the reduction of any damage of the constituent members and therefore, this may result in an increase in the number of reuse times of the constituent members such as an adhesion preventive plate and the like.

Brief Description of the Drawings

[0019]

[Figure 1]: Fig. 1 is a graph showing simulated deposit film-peeling time (hour) (peelability) observed for an Al

alloy-sprayed film (heat treatment: $250^{\circ}\text{C}\times 100\text{hr}$ (hours)) having the composition described in Reference Example 1.

[Figure 2]: Fig. 2 is a graph showing simulated deposit film-peeling time (hour) observed for an Al alloy-sprayed film (heat treatment: $270^{\circ}\text{C}\times 150\text{hr}$) having the composition described in Reference Example 2.

[Figure 3]: Fig. 3 is a graph showing simulated deposit film-peeling time (hr) observed for an Al alloy-sprayed film (heat treatment: $250^{\circ}\text{C}\times 150\text{hr}$) having the composition described in Example 1.

[Figure 4]: Fig. 4 is a graph showing simulated deposit film-peeling time (hr) observed for an Al alloy-sprayed film (heat treatment: $300^{\circ}\text{C}\times 150\text{hr}$) having the composition described in Example 2.

[Figure 5]: Fig. 5 is a schematic perspective view (a) for illustrating the method for determining the strength (maximum point stress (N/mm^2)) of Al alloy-sprayed films (heat treatment: untreated; $200^{\circ}\text{C}\times 150\text{hr}$; $250^{\circ}\text{C}\times 150\text{hr}$; $300^{\circ}\text{C}\times 150\text{hr}$) having the compositions described in Example 3 and a graph (b) showing the maximum point stresses observed for the Al alloy-sprayed films.

Mode for Carrying Out the Invention

[0020]

When forming a thin film according to a variety of film deposition techniques such as the sputtering technique while using a film deposition apparatus, the interior of the film deposition chamber of the apparatus is exposed to repeated thermal history. For this reason, the surface of constituent members arranged within the film deposition chamber such as an adhesion preventive plate, which are coated with the

water-reactive Al alloy-sprayed film according to the present invention, are likewise suffered repeated thermal history. Accordingly, it would be necessary that the Al alloy-sprayed film immediately after the formation thereof and prior to experiencing any thermal history should be stable and capable of being easily handled and that the Al alloy-sprayed film to which a deposited film is inevitably adhered and which has gone through thermal history attributable to the film deposition process should likewise have solubility (activity) which allows easy removal of the deposited film from base materials and should be stable. In the case of the water-reactive Al alloy-sprayed film according to the present invention, it can satisfactorily meets the requirements for solubility and stability.

15 [0021]

Since the upper temperature limit of the thermal history within the foregoing film deposition chamber is, for instance, about 300 to 350°C for the sputtering technique, the vacuum deposition technique, the ion plating technique, the CVD technique and the like, it would generally be sufficient, for practical purpose, that the Al alloy-sprayed film, which has been subjected to thermal history at a temperature of up to 300°C, has reactivity with water. According to the present invention, however, high reactivity with water would be ensured even an Al alloy-sprayed film which has been subjected to thermal history at a higher temperature of up to about 350°C.

[0022]

The following are the description of embodiments according to the present invention.

An Al alloy-sprayed film consisting of an Al composite material to which Bi is added (for instance, Al-1wt% Bi) comprises Al in which Bi is uniformly and highly dispersed and therefore, it may easily undergo a reaction in a moisture-containing atmosphere (at a temperature of, for instance, 80°C) such as water, water vapor, an aqueous solution or the like and may thus be dissolved therein. Bi may affect the number of reaction sites. If allowing the Al alloy-sprayed film to stand in the atmosphere for 10 hours after the formation thereof according to the thermal spraying, however, the film has such a disadvantage that it easily reacts with moisture in the air and causes a powdering phenomenon. For this reason, it is needed to add Si to the Al alloy-sprayed film in order to ensure the stability of the sprayed film after the formation thereof as will be detailed below.

[0023]

In general, the electrochemical potential difference between Al and Bi is extremely high in an Al-Bi system, but the ionization of Al does not proceed if the natural oxide film of Al is present thereon. However, once the natural oxide film is broken and Al is directly linked with Bi, the potential difference established between them may abruptly accelerate the ionization of Al. On this occasion, Bi atoms are present, as it is, in Al crystal grains in their highly dispersed condition without undergoing any chemical change. Bi has a low melting point (271°C) and never forms a solid solution with Al. Accordingly, a material, obtained by melting Al and Bi in such a manner that the resulting molten material has uniform composition, while taking care of the

difference in density between Al and Bi, can thermally be sprayed on a base material according to the thermal spraying method to thus give a desired film because of the quenching and solidification of the material as well as the compression effect thereof.

[0024]

The Bi thus added is highly dispersed in Al crystal grains through the thermal spraying process and it is kept in a state directly contacting with Al. Since Bi does not form any stable layer with Al, the Al/Bi boundary holds a high energy and undergoes a vigorous reaction with water within a moisture-containing atmosphere on the surface contacting with moisture. Moreover, the reaction products mainly comprising AlOOH are finely pulverized or micronized and dissipated or scattered in the liquid without forming a film on the surface due to the mechanical action originated from the expansion of H₂ bubbles generated, in addition to the highly dispersed condition of Bi as an added element and thus the solubilizing reaction persistently and explosively proceeds at the successively renewed reaction boundary.

[0025]

As has been described above, an Al alloy-sprayed film consisting of an Al-Bi composite material, which is in the state just after being formed through a thermal spraying process, has an extremely high activity and accordingly, the sprayed film is satisfactory in terms of the solubility in a moisture-containing atmosphere, but it is difficult to handle the same. In addition, the reactivity (solubility) of the thermally sprayed film after experiencing thermal history is not reduced so much.

[0026]

The addition of a predetermined amount of Si to the foregoing Al-Bi composite material results in the reduction of the activity of the Al alloy-sprayed film produced from the resulting Al composite material, this makes the handling of the Al alloy-sprayed film easy, further the Al alloy-sprayed film after experiencing thermal history is highly improved in its activity and the film can manifest or express high solubility (activity) in a moisture-containing atmosphere. However, the Al alloy-sprayed film may sometimes undergo a powdering phenomenon depending on the composition ratio of Bi and Si, when the film is just only allowed to stand in the atmosphere for 2 to 3 hours after subjecting it to thermal history. Accordingly, in such case, the film after experiencing thermal history and prior to subjecting it to its peeling treatment is preferably stored in a dry atmosphere (a vacuum atmosphere may likewise be used) in order to prevent the occurrence of a reaction with the moisture in the atmosphere.

[0027]

With regard to the addition of Si, the effect of added Si on the stability of a sprayed film was investigated using compositions consisting of Al-1wt% (% by mass) Bi-1.5wt% Si, Al-1wt% Bi-2wt% Si, and Al-1wt% Bi-2.5wt% Si. Using A5052 and SUS304 as base materials, the foregoing compositions were thermally sprayed on individual base materials (thermal spraying method: wire flame spraying). As a result, it was confirmed that the stability of the sprayed film is improved even after the thermal spraying and after allowing to stand in the atmosphere for 300 hours and that the sprayed film

does not cause any powdering phenomenon. However, when this sprayed film was heat-treated ($150^{\circ}\text{C}\times 1$ hour) and then allowed to stand in the atmosphere, it was verified that the film undergoes a powdering phenomenon and that this sprayed film is thus activated through such a heat-treatment.

[0028]

As will be described in the following Reference Example 1, when adding Ce to an Al-Bi-Si-Ti system, the time required for the peeling of the resulting sprayed film (simulated deposit film) is further reduced. The term "simulated deposit film" herein used means a film which simulates an inevitable deposit film of a metal or a metal compound which is deposited on the constituent members of a film deposition apparatus during an actual film deposition process, wherein the simulated deposit film is prepared by depositing Al having a purity of 4N on an Al alloy-sprayed film composed of, for instance, Al-Bi-Si-Ti or Al-Bi-Si-Ti-Ce according to the flame spraying method. Thus, the addition of Ce, which is a metal having a standard electrode potential lower than that of Al, results in the reduction of the potential observed for the whole sprayed film and it would be found that the activation by this potential reduction would improve the peelability of the Al alloy-sprayed film after the heat-treatment at a high temperature (250°C) attributable to the process temperature. Moreover, with regard to the Al alloy-sprayed film consisting of an Al-Bi-Si-Ti-Ce system, the film was allowed to stand in a constant temperature furnace at predetermined temperature and humidity for a predetermined time period and then the number of surface particles was determined according to the usual method. As

a result, it was confirmed that the particle number thus detected is quite small, the particle formation is thus suppressed or controlled and the desired stability can be imparted to the sprayed film.

5 [0029]

In addition, as will be described in the following Reference Example 2, in the case of an Al-Bi-Si-Ti-Ce system, the resulting sprayed film was subjected to a heat-treatment at a predetermined temperature for a predetermined time period. As a result, it was confirmed that the time required for peeling the sprayed film (simulated deposit film) is substantially reduced and that it can easily be removed.

[0030]

Preferred embodiments according to the present invention will now be described, while referring to a water-reactive Al composite material consisting of an Al-Bi-Si-Ti-Ce-Mg system.

[0031]

A water-reactive Al alloy-sprayed film is produced by forming a film on the surface of a base material to be processed within a predetermined atmosphere according to the thermal spraying method, while using the aforementioned water-reactive Al composite material comprising Al in which Bi, Si, Ti, Ce and Mg are uniformly distributed. The resulting water-reactive Al alloy-sprayed film comprises Al crystal grains which include individual metal crystal grains in the state uniformly and highly dispersed therein.

[0032]

The foregoing Al alloy-sprayed film is prepared, for instance, according to the following procedures:

Al, Bi, Si, Ti, Ce and Mg are provided, followed by incorporating, into Al, on the basis of the mass of Al, Bi in an amount of not less than 0.2% by mass and not more than 2% by mass, preferably not less than 0.5% by mass and not
5 more than 2% by mass; Si in an amount of not less than 1.5% by mass and not more than 8% by mass; Ti in an amount of not less than 0.2% by mass and not more than 4% by mass; Ce in an amount of not less than 0.2% by mass and not more than 2% by mass; and Mg in an amount of not less than 0.2% by mass
10 and not more than 2% by mass, uniformly distributed, through melting, these metals in Al, thereafter processing the resulting Al composite material in the form of a rod or a wire, then covering, with the Al composite material, a base material such as a component for a film deposition chamber,
15 for example, an adhesion preventive plate used in a film deposition apparatus by spraying the composite material on the surface of the base material according to, for instance, the wire flame spraying method, while using the foregoing rod or wire as a thermal spray material, then quenching and
20 solidifying the sprayed film consisting of the material. Thus, an intended base material provided thereon with a desired water-reactive Al alloy-sprayed film can be produced. The Al alloy-sprayed film thus prepared is a film constituted by Al crystal grains in which Bi is present in such a state
25 that it is uniformly and highly dispersed in the Al crystal grains, as has been described above.

[0033]

In the case of the water-reactive Al alloy-sprayed film prepared by adding desired amounts of the aforementioned
30 metals to an Al-Bi system in a manner discussed above, it is

possible to control the solubility of the film, per se, formed by the thermal spraying method and accordingly, it would become possible to prevent the sprayed film from undergoing a reaction with moisture within the atmosphere and the film can thus be handled with ease.

[0034]

When immersing the base material covered with the aforementioned Al alloy-sprayed film or the same base material which has been subjected to a heat-treatment in a moisture-containing atmosphere such as water, water vapor, an aqueous solution or the like, for instance, immersing the same in hot water of a predetermined temperature, the reaction of the film with water is initiated immediately after the immersion along with the generation of hydrogen gas and if the reaction further proceeds, the water is blackened and finally the sprayed film is removed and is completely dissolved in water, while leaving Al, Bi, Si, Ti, Ce and Mg in the hot water in the form of precipitates. The higher the temperature of water, the more this reaction vigorously proceeds. It is sufficient that the temperature of the moisture-containing atmosphere is, for instance, 40 to 130°C and preferably 80 to 100°C.

[0035]

The foregoing thermally sprayed film has been described with reference to one produced according to the flame spraying method using a material in the form of a rod or a wire, but the film can likewise be produced according to other flame spraying methods or even according to the arc spraying and plasma spraying methods. In the present invention, a thermally sprayed film is formed by spraying

the aforementioned raw materials on the surface of a base material under known process conditions according to these thermal spraying methods and then quenching and solidifying the resulting sprayed film.

5 [0036]

As has been described above, if using constituent members, whose surface is covered with the foregoing water-reactive Al alloy-sprayed film, as those for a film deposition chamber, for instance, an adhesion preventive plate and a shutter which are arranged or disposed within the film deposition chamber of a film deposition apparatus, the inevitably adhered film attributable to film deposition materials and formed on the constituent members for the film deposition chamber can easily be removed from the constituent members after repeatedly using them in the film deposition processes over desired times and accordingly, the valuable metals present therein can be recovered with ease.

[0037]

In this case, used herein as a peeling liquid is not any chemical agent, but mere water such as pure water, water vapor or an aqueous solution and therefore, this would permit the protection of a constituent member for a film deposition chamber such as an adhesion preventive plate from being damaged through the dissolution thereof and the number of reuse times of these constituent members dramatically increases as compared with that observed when using a chemical agent. In addition, any chemical agent is not used and therefore, the processing cost can dramatically be reduced and this would also result in the environmental protection. Furthermore, most of film deposition materials

which may undergo the adhesion to the component for a film deposition chamber such as an adhesion protective plate are never dissolved in water and accordingly, there is such a merit that the adhered film can be recovered in the form of a solid having the same composition and shape as those of the film deposition materials. Moreover, there is such a merit that the range of film deposition materials which can be recovered is expanded because of not only the dramatic reduction of the processing cost, but also the simplification of the procedures required for the recovery. For instance, if the water-reactive Al alloy-sprayed film according to the present invention is applied onto the constituent members for a film deposition chamber such as an adhesion preventive plate and in the case where the film deposition materials are expensive metals such as precious metals and rare metals, the film inevitably adhered to the constituent members for the film deposition chamber during the film deposition procedures and consisting of the film deposition materials can be removed by dipping the constituent members provided with the adhered film in water or spraying water vapor on the constituent members and therefore, precious metals, rare metals and the like can be recovered without being accompanied by any contamination. Thus the recovery cost is not expensive and the film deposition materials can be recovered, while maintaining high quality of these materials.

[0038]

The present invention will hereunder be described in more detail with reference to the following Reference Examples and Working Examples.

(Reference Example 1)

Al, Bi, Si and Ti were used, further Ce was used as an additive and there was investigated the effect of the addition of Ce on the time (hour) required for the removal of sprayed films formed from the following systems each having a composition likewise specified below. The added amounts are expressed in terms of percent by weight (wt%) on the basis of the weight of the Al. Used as a control was a thermally sprayed film composed of Al-3wt% In-0.4wt% Si-0.2wt% Ti (see Patent Official Gazette No. 5,517,371) as one of the Al-In system, obtained according to the wire flame spraying method

- Al-1wt% Bi-3wt% Si-1wt% Ti (number of N:3);
- Al-1wt% Bi-3wt% Si-2wt% Ti (number of N:3);
- Al-1wt% Bi-3wt% Si-1wt% Ti-0.2wt% Ce (number of N:3);
- Al-1wt% Bi-4wt% Si-1wt% Ti (number of N:3);
- Al-1wt% Bi-4wt% Si-2wt% Ti (number of N:3).

[0039]

An Al composite material was produced by blending Al, Bi, Si, Ti and Ce in the ratio specified above and uniformly distributing, through melting, every metals other than Al in the Al and then processing the resulting Al composite material into a wire. An Al alloy-sprayed film was then formed by spraying the resulting Al composite material on the surface of a base material (A5052) consisting of Al in the atmosphere according to the molten wire type flame spraying (wire flame spraying) method (heat source: C₂H₂-O₂ gas; temperature: about 3,000°C; spraying gun: Model 12E manufactured by Sulzer Metco, Inc.), while using the wire-shaped Al composite material prepared above as a thermal spray material, and subsequently a simulated deposit film

was formed on the sprayed film.

[0040]

Each of the Al alloy-sprayed film thus produced and provided with the simulated deposit film was subjected to a heat treatment at a temperature of 250°C (carried out in the atmosphere, for 100 hours; subjected to furnace cooling), in place of the thermal history to which the deposit film would be exposed during the film deposition process. The solubility of each sprayed film was then investigated by dipping the base material provided with the sprayed film, which had been subjected to the heat-treatment, in 300 mL of pure water maintained at a temperature of $80 \pm 1^\circ\text{C}$ and then determining the time (hr) required for the peeling of each sprayed film (the simulated deposit film). The results thus obtained are plotted on Fig. 1. In Fig. 1, the peeling time (hr (hour)) observed for the simulated deposit film is plotted as ordinate.

[0041]

As will be apparent from Fig. 1, the sprayed film of the Al-Bi system is removed or peeled within a short period of time as compared with that observed for the Al-In system (control) and this indicates that the peelability of the former is high. Moreover, in the case of the sprayed film composed of the Al-Bi-Si-Ti system, the time required for peeling the Al alloy-sprayed film (the simulated deposit film) is reduced as the amount of Ti is increased and this indicates that the peelability of the sprayed film is high. Further, it is found that when adding Ce to this Al-Bi system, the peeling time observed for the resulting Al alloy-sprayed film (the simulated deposit film) is further reduced. Thus,

it is evident that the addition of Ce, which is a metal having a standard electrode potential lower than that observed for Al, would result in the reduction of the potential with respect to the entire sprayed film and that the peelability of the Al alloy-sprayed film obtained after being subjected to a high temperature (250°C) heat-treatment attributable to the process temperature would be improved because of the activation through this reduction in the potential.

10 [0042]

In addition, an Al alloy-sprayed film consisting of the foregoing control composition and an Al alloy-sprayed film composed of Al-1wt% Bi-3 to 4wt% Si-1 to 2wt% Ti-0.2wt% Ce produced in the same manner as described above were investigated for the stability thereof by allowing them to stand in a constant temperature furnace at 40°C and 90% R.H. for 108 hours and then determining the number of surface particles (measurement environment: clean room; class: 1,000; measuring device: QIII MAX available from Pentagon Technologies, Inc.). As a result, the number of particles detected for the sprayed film consisting of the control composition was found to be about 3,800 particles/cm² for a particle size of 0.3µm, and about 2,400 particles/cm² for a particle size of 0.5µm, while that detected for the sprayed film composed of Al-1wt% Bi-3 to 4wt% Si-1 to 0.2wt% Ti-0.2wt% Ce was found to be not more than about 400 particles/cm² for a particle size of 0.3µm, and not more than about 200 particles/cm² for a particle size of 0.5µm. Thus it was confirmed that the Al alloy-sprayed film according to the present invention permits the inhibition of particle

generation and the acquirement of a high stability.

[0043]

(Reference Example 2)

In this Reference Example, the same processes used in
5 Reference Example 1 were repeated except that a heat-
treatment at 270°C (carried out in the atmosphere, for 150
hours; subjected to furnace cooling) was substituted for the
heat-treatment (250°C×100) used in Reference Example 1, to
be applied to every corresponding Al alloy-sprayed films
10 (simulated deposit films) having the same compositions
specified in Reference Example 1 and prepared in the manner
used therein. The base materials each provided with the
sprayed film after being subjected to the heat-treatment
were investigated for their solubility by dipping them in
15 300 mL of pure water maintained at a temperature of 80±1°C,
and then determining the time (hour) required for peeling
each sprayed film (simulated deposit film). The results
thus obtained are plotted on Fig. 2. In Fig. 2, the peeling
time (hr) observed for the simulated deposit film is plotted
20 as ordinate.

[0044]

As will be clear from Fig. 2, the simulated deposit
films could not be removed in the case of the control film
(Al-In-Si-Ti) and the film composed of Al-Bi-Si-Ti even after
25 3 hours, but when Ce was added to this Al-Bi-Si-Ti system,
the simulated deposit film could be removed within not more
than 0.5 hours. It is thus verified that the addition of Ce
would permit the improvement in the peelability of the Al
alloy-sprayed film after being subjected to a heat-treatment
30 at a high temperature (270°C) attributable to the process

temperature.

Example 1

[0045]

Al, Bi, Si, Ti, Ce and Mg were used for forming an Al
5 composite material and there was investigated the effect of
the addition of Ce, Mg to a composite material, having the
following composition, on the time (hour) required for
peeling the resulting Al alloy-sprayed film. The added
amounts are expressed in terms of percent by weight (wt%) on
10 the basis of the weight of the Al. Used herein as a control
was a film composed of Al-3wt% In-0.4wt% Si-0.2wt% Ti (see
Patent Official Gazette No. 5,517,371) as one of the Al-In
system.

• Al-1wt% Bi-3wt% Si-1wt% Ti-0.2wt% Ce-0.5wt% Mg (number of
15 N:3).

[0046]

Al, Bi, Si, Ti, Ce and Mg were blended in the ratio
specified above, then uniformly dispersing, through melting,
every metals other than Al in the Al to form an Al composite
20 material, and thereafter the resulting composite material
was processed into a wire to thus give a thermal spray
material. Then an Al alloy-sprayed film was formed by
spraying the resulting Al composite material on the surface
of a base material (A5052) composed of Al in the atmosphere
25 according to the molten wire type flame spraying (heat
source: C₂H₂-O₂ gas; temperature: about 3,000°C; spraying gun
used: Model 12E), while using the thermal spray material
prepared above (in the case of the control, the thermal spray
material was prepared in the same manner), and then a
30 simulated deposit film was formed in the same manner used

above. Each of the sprayed films (the simulated deposit film) thus produced was subjected to a heat treatment at a temperature of 250°C (carried out in the atmosphere, for 150 hours; subjected to furnace cooling), in place of the thermal history attributable to the film deposition process. The solubility of each sprayed film was investigated by dipping the base material provided with the sprayed film, after being subjected to the foregoing heat-treatment, in 300 mL of pure water maintained at a temperature of 80±1°C and then determining the time (hour) required for the peeling of each sprayed film (the simulated deposit film). The results thus obtained are plotted on Fig. 3. In Fig. 3, the peeling time (hr (hour)) observed for the simulated deposit film is plotted as ordinate.

[0047]

As will be clear from Fig. 3, the simulated deposit film could not be removed in the case of the control film composed of the Al-In system even after 3 hours, but in the case of the present invention, the simulated deposit film could be removed within not more than one hour without being accompanied by any problems. It is thus apparent that the addition of Ce would permit the improvement, in the peelability, of the Al alloy-sprayed film after being subjected to a heat-treatment at a high temperature (250°C) attributable to the process temperature.

[0048]

Moreover, when the Al alloy-sprayed film composed of Al-1wt% Bi-3wt% Si-1wt% Ti-0.2wt% Ce free of any added Mg is also heat-treated at 300°C for one hour and then allowed to stand in the atmosphere for a long period of time, the

sprayed film sometimes undergoes powdering on the surface thereof. However, it was confirmed that the addition of 0.2wt% Mg showed an effect of inhibiting the occurrence of any powdering, while when 0.5wt% Mg was added, any powdering was not detected even after allowing the film to stand for more than 100 hours. Thus, it was confirmed that the addition of Mg would permit the stabilization of the resulting Al alloy-sprayed film and the inhibition of the occurrence of any powdering, even after the film was subjected to a heat-treatment.

Example 2

[0049]

In this Example, the same processes used in Example 1 were repeated except for the following difference: In Example 1, the heat-treatment at 250°C (carried out in the atmosphere, for 150 hours; subjected to furnace cooling) applied to each of the resulting Al alloy-sprayed films was substituted for thermal history originated from the film deposition process, while in this Example, a heat-treatment at 300°C (carried out in the atmosphere, for 150 hours; subjected to furnace cooling) was substituted for the heat-treatment used in Example 1. The results thus obtained are plotted on Fig. 4. In Fig. 4, the peeling time (hr (hour)) observed for the simulated deposit film is plotted as ordinate.

[0050]

As will be clear from Fig. 4, the simulated deposit film could not be removed in the case of the control film composed of the Al-In system even after 3 hours, but in the case of the present invention, the simulated deposit film could be removed within about 1.5 hours without accompanied

by any problems. It is thus apparent that the addition of Ce would permit the improvement in the peelability of the Al alloy-sprayed film after being subjected to a heat-treatment at a high temperature (300°C).

5 **Example 3**

[0051]

Al composite materials were prepared using Al, Bi, Si, Ti, Ce and Mg, and there was investigated the effect of the addition of Ce, Mg to the composite materials having the compositions specified below while taking into consideration the presence or absence of a heat-treatment, a variety of temperatures used in the heat-treatments, i.e. the effect of the thermally sprayed film on the strength thereof (the maximum point stress: N/mm²). The added amounts thereof are expressed in terms of percent by mass on the basis of the mass of the Al used. Used herein as a control was a film composed of Al-3wt% In-0.4wt% Si-0.2wt% Ti (see Patent Official Gazette No. 5,517,371) as one of the Al-In system.

• Al-1wt% Bi-3wt% Si-1wt% Ti-0.2wt% Ce-0.5wt% Mg (heat-treatment: untreated; number of N:3);

• Al-1wt% Bi-3wt% Si-1wt% Ti-0.2wt% Ce-0.5wt% Mg (heat-treatment: 200°C×150hr; number of N:3);

• Al-1wt% Bi-3wt% Si-1wt% Ti-0.2wt% Ce-0.5wt% Mg (heat-treatment: 250°C×150hr; number of N:3);

• Al-1wt% Bi-3wt% Si-1wt% Ti-0.2wt% Ce-0.5wt% Mg (heat-treatment: 300°C×150hr; number of N:3).

[0052]

Al, Bi, Si, Ti, Ce and Mg were blended at the rates specified above and the additive metals were uniformly dispersed, through melting, in the Al to thus give

corresponding Al composite materials. Each of the resulting Al composite materials was processed in the form of a wire to give each corresponding thermal spray material (in the case of the control, the thermal spray material was prepared in the same manner). Then the corresponding thermally sprayed film was produced by spraying one of the foregoing Al composite materials on the surface of a coin-shaped sample (A5052) in the atmosphere according to the molten wire type flame spraying (heat source: $C_2H_2-O_2$ gas; temperature: about 3,000°C; spraying gun used: Model 12E), while using the wire-like thermal spray material prepared above. Each of the sprayed films thus produced was subjected to the following heat-treatments: 200°C×150hr; 250°C×150hr; and 300°C×150hr (carried out in the atmosphere; subjected to furnace cooling), in place of the thermal history attributable to the film deposition process. Each of the coin-shaped sample on which the aforementioned Al alloy-sprayed film had been deposited was fixed to a tensile test jig made of SUS304 with an adhesive as shown in Fig. 5(a), followed by carrying out the tensile test using AUTOGRAPH manufactured by SHIMADZU Corporation attached to the tensile test jig, to which the coin sample had been adhered, at a tensile rate of 1 mm/min to thereby rupture the sprayed film and to thus determine the maximum point stress. The rupture of the film was mainly caused at the boundary between the sprayed film and the adhesive and the rupture was partially caused within the sprayed film as well. The coin sample provided with the sprayed film after being subjected to a heat-treatment was also examined for the maximum point stress: N/mm², to thus investigate the sprayed film for the strength thereof. The

results thus obtained are plotted on Fig. 5(b). In Fig. 5(b), the maximum point stress: N/mm^2 is plotted as ordinate. [0053]

As will be clear from Fig. 5(b), when compared with the Al alloy-sprayed film composed of the Al-In system used as the control, the Al alloy-sprayed film having the composition according to the present invention showed the strength almost identical to that observed for the control when it was free of any heat-treatment, but the strength thereof was increased after being subjected to a heat-treatment. Thus, the addition of Ce, Mg permits the improvement in the strength of the Al alloy-sprayed film after the heat-treatment at a high temperature attributable to the process temperature and the addition of Si, Ti likewise improves the strength of the Al alloy-sprayed film.

Example 4

[0054]

The compositions with respect to Al, Bi, Si, Ti, Ce and Mg disclosed in Example 1 were set as follows: Al-0.2wt% Bi-1.5wt% Si-0.2wt% Ti-0.2wt% Ce-0.2wt% Mg (number of N: 3) and Al-1wt% Bi-4wt% Si-2wt% Ti-1wt% Ce-0.5wt% Mg (number of N: 3), then the same procedures for the wire flame spraying described in Example 1 were repeated using these two samples and as a result, it was confirmed that the peelability observed for all of the Al alloy-sprayed films are identical to one another. Furthermore, Al alloy-sprayed films having the same compositions described above were also examined for their strength and as a result, it was proved that they had almost the same strength.

Example 5

[0055]

One cycle of Mo film-formation was carried out using a sputtering apparatus equipped with an adhesion preventive plate whose surface had been covered with a sprayed film (film thickness: 200 μ m) composed of the Al-1wt% Bi-3wt% Si-1wt% Ti-0.2wt% Ce-0.5wt% Mg composite material prepared in Example 1. At this stage, the sputtering operation was carried out under the following conditions: sputtering time: 150 hours; sputtering temperature: 200°C; Mo film thickness: about 1 mm. This adhesion preventive plate on which an Mo film had been deposited was removed from the apparatus and the surface of the plate was observed. As a result, it was proved that any powdering phenomenon was not caused even after the sputtering and there was not observed any change in the stability of the sprayed film. Then this adhesion preventive plate was treated with warm water of 80°C and it was found that the sprayed film was dissolved therein after about 5 minutes and the adhered Mo film was peeled off from the adhesion preventive plate. For this reason, Mo as a film deposition material could easily be recovered. At this stage, AlOOH was precipitated in the warm water.

[0056]

Moreover, the film deposition according to the sputtering was also performed using Ti instead of Mo. In this case, the sputtering was conducted under the same conditions used in the case of the Mo sputtering to thus give a film having a thickness of about 1 mm. The adhesion preventive plate provided with a Ti film adhered thereto was detached from the apparatus and the surface thereof was observed. As a result, it was found that any powdering

phenomenon was not caused even after the sputtering and that there was not observed any change in the stability of the sprayed film. Then this adhesion preventive plate was treated with warm water of 80°C and it was found that the sprayed film was dissolved therein after about 10 minutes and that the adhered Ti film was peeled off from the adhesion preventive plate. For this reason, Ti as a film deposition material could easily be recovered.

Industrial Applicability

10 [0057]

If covering, with an Al alloy-sprayed film composed of the water-reactive Al composite material according to the present invention, the surface of a component for a film deposition chamber disposed in a vacuum film deposition apparatus used for forming a thin film composed of a metal or a metal compound according to the sputtering, vacuum vapor deposition, ion plating, CVD techniques or the like, any inevitably adhered film which may be adhered to the surface of the component for the film deposition chamber during film deposition processes can be removed and recovered in a moisture-containing atmosphere. Therefore, the present invention can be used to increase the number of reuse times of constituent members for film deposition chambers and to recover film deposition materials containing valuable metals, in fields in which these film deposition apparatuses are employed, for instance, in the technical fields of manufacturing semiconductor elements and electronics-related equipment.

Claims

What is claimed is:

1. A water-reactive Al composite material for thermal spraying, characterized in that it comprises Al to which are added, on the basis of the weight of the Al, Bi in an amount of not less than 0.2% by mass and not more than 2% by mass; Si in an amount of not less than 1.5% by mass and not more than 8% by mass; Ti in an amount of not less than 0.2% by mass and not more than 4% by mass; Ce in an amount of not less than 0.2% by mass and not more than 2% by mass; and Mg in an amount of not less than 0.2% by mass and not more than 2% by mass.
2. A method for preparing a water-reactive Al alloy-sprayed film, characterized in that it comprises the steps of melting a material comprising Al to which are added, on the basis of the weight of Al, Bi in an amount of not less than 0.2% by mass and not more than 2% by mass; Si in an amount of not less than 1.5% by mass and not more than 8% by mass; Ti in an amount of not less than 0.2% by mass and not more than 4% by mass; Ce in an amount of not less than 0.2% by mass and not more than 2% by mass; and Mg in an amount of not less than 0.2% by mass and not more than 2% by mass, in such a manner that the composition of the resulting material becomes uniform; spraying the resulting molten material on the surface of a substrate; and then quenching and solidifying the sprayed molten material to thus form a film.
3. A water-reactive Al alloy-sprayed film, characterized in that it consists of a water-reactive Al composite material for thermal spraying as set forth in claim 1.
4. A component for a film deposition chamber used in a film

deposition apparatus, characterized in that it is provided, on the surface thereof, a water-reactive Al alloy-sprayed film which consists of a water-reactive Al composite material for thermal spraying as set forth in claim 1.

- 5 5. The component for the film deposition chamber as set forth in claim 4, characterized in that the component is an adhesion preventive plate, a shutter or a mask.