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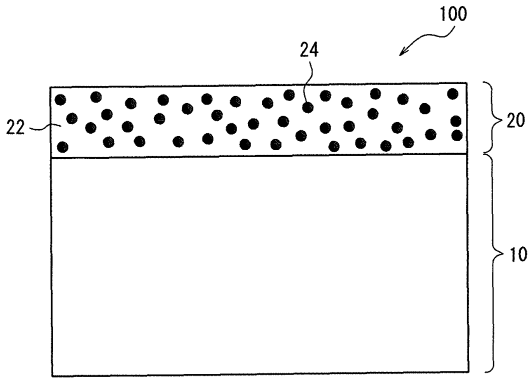
(54) CERMET POWDER, PROTECTIVE FILM-COATED MEMBER AND METHOD FOR PRODUCING SAME, AND ELECTROPLATING-BATH ROLL AND METHOD FOR PRODUCING SAME

(57) Disclosed is a cermet powder that enables preparation of a cermet coating having both high wear resistance and high corrosion resistance against a strong acid having a pH of less than 1. The disclosed cermet powder contains tungsten carbide particles in an amount of 40 mass% or more; molybdenum carbide particles in an amount of 10 mass% to 40 mass%; and Ni or a Ni alloy as a matrix metal, wherein the cermet powder further contains chromium, either as a carbide or a metal or alloy element contained in the matrix metal, in an amount of 8 mass% or more.

FIG. 1



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Description

TECHNICAL FIELD

[0001] The present disclosure relates to a cermet powder, a protective-coating-coated member and a method of producing the same, and an electroplating-bath-immersed roll and a method of producing the same.

BACKGROUND

[0002] Conventionally, as a method of producing a conductor roll used in an electroplating bath, the following have been proposed. JPH1198460A (PTL 1) describes a method in which plasma arc spraying is performed on a surface of a carbon steel roll using as a thermal spraying material an alloy containing Co or Ni as a main component and an additive of Cr, C, Fe, Mo, or the like under a low-pressure oxygen-free atmosphere, and the coating is then subjected to a hot melt treatment by plasma arc heating under the same atmosphere to form a nonporous thermal sprayed coating.

[0003] JPH5295592A (PTL 2) describes a method in which a thermal-spray coated layer is formed by thermal spraying a mixed powder composed of a carbide cermet powder and a C-containing nickel chromium alloy powder on the surface of a carbon-steel roll body portion, then causing redeposition of carbide by heating the thermal spray coating layer to form a redeposited-carbide-dispersed thermal sprayed coating, and subsequently shrink-fitting the roll body portion to the outside of the roll base member.

[0004] JP200288461A (PTL 3) describes a method of producing a conductor roll having enhanced corrosion resistance, in which a mixed powder composed of WC-Ni cermet and the balance consisting of a Ni-base self-fluxing alloy is thermal sprayed on the surface of a SS-400 roll, and thereafter a remelting treatment is carried out to form a coating layer.

[0005] JP2006183107A (PTL 4) describes a method of producing a conductor roll, in which a self-fluxing alloy thermal sprayed layer containing WC cermet is formed on the surface of a SS-400 roll and a WC cermet coating is further formed thereon.

CITATION LIST

Patent Literature

[0006]

PTL 1: JPH1198460A
PTL 2: JPH5295592A
PTL 3: JP200288461A
PTL 4: JP2006183107A

SUMMARY

(Technical Problem)

[0007] In PTL 1, a plating solution of a strong acid having a pH of less than 1 has the problem that the plating solution infiltrates from the surface of the coating after continuous use, causing the adhesion between the roll substrate and the thermal sprayed coating to decrease and the coating to peel off from the surface of the substrate. In fact, the technique of PTL 1 is not implemented under severe circumstances such as a pH below 1, in which the implementation conditions are only demonstrated in the current density range as low as 5 A/dm^2 to 20 A/dm^2, and the operation period is as short as 1,000 hours. This means that the technique of PTL 1 fails to address a long-term operation, such as one month continuous operation. In addition, since the thermal melting treatment of the coating is performed after thermal spraying, there is a problem of increased manufacturing cost.

[0008] Again, in PTL 2, a plating solution of a strong acid having a pH of less than 1 has the problem that the plating solution infiltrates from the surface of the coating after continuous use, causing the adhesion between the roll substrate and the thermal sprayed coating to decrease and the coating to peel off from the surface of the substrate. In addition, the edge of the roll is acid corroded by the plating solution, leading to the problem of fragments lowering the product yield. It is also necessary to carry out remelting treatment on the roll after thermal spraying, causing a problem that the time and cost associated with roll regeneration including shrink-fitting are increased.

[0009] Also in PTL 3, a plating solution of a strong acid having a pH of less than 1 has the problem that the plating solution infiltrates from the surface of the coating after continuous use, causing the adhesion between the roll substrate and the thermal sprayed coating to decrease and the coating to peel off from the surface of the substrate. It is also necessary to carry out remelting treatment on the roll after thermal spraying, causing a problem that the time and cost associated with roll regeneration are increased. In addition, when applying this coating to a stainless steel roll, the remelting treatment causes cracking at the crystal grain boundary due to heating of the stainless steel, and the roll is damaged. For this reason, carbon steel having low corrosion resistance has to be used, leading to the problem of fragments of acid-corroded carbon steel lowering the product yield.

[0010] Also in PTL 4, a plating solution of a strong acid having a pH of less than 1 has the problem that the plating solution infiltrates from the surface of the coating after continuous use, causing the adhesion between the roll substrate and the thermal sprayed coating to decrease and the coating to peel off from the surface of the substrate. Actually, in the test of acid corrosiveness by immersion in a plating solution in PTL 4, the pH is 3.0, and no test was conducted under severe environments such as a pH below 1. It is also necessary to carry out remelting treatment on the roll after thermal spraying, causing a problem that the time and cost associated with roll regeneration are increased. In addition, when applying this coating to a stainless steel roll, the remelting treatment causes cracking at the crystal grain boundary due to heating of the stainless steel, and the roll is damaged. For this reason, carbon steel having low corrosion resistance has to be used, leading to the problem of fragments of acid-corroded carbon steel lowering the product yield.

[0011] As described above, the conventional conductor rolls are primarily characterized in that carbon steel is used as the roll material, and for the purpose of preventing reaction of the carbon steel with the plating solution, a coated layer of a NiCr-based alloy is formed on the roll surface. This coated layer is characterized by containing a carbide (or cermet) mainly composed of WC for the purpose of preventing wear due to rubbing against a steel sheet. This may greatly reduce reaction and wear in an acidic plating bath of $pH \geq 1$, secure the roll life, and reduce the defective rate.

[0012] However, in such a conventional conductor roll, in the strong acid plating bath with $pH < 1$, the acid corrosion amount of the carbon steel itself greatly increases, and in addition, the corrosion resistance of the coated layer itself containing carbide becomes insufficient, raising the problem of the effect obtained being small for the cost involved in the production of the roll. That is, it is difficult to achieve both high wear resistance and high corrosion resistance against a strong acid having a pH of less than 1 in those rolls obtained by the conventional technique and conventional surface treatment.

[0013] Further, it was found that in a conventional product having a thermal sprayed coating on the carbon steel roll base member, the thermal sprayed coating and the carbon steel roll base member are damaged due to acid corrosion, and some fragments jump into the plating product, resulting in defects such as pressing flaw and thus lower product yield. In addition, in a general tin electroplating process, it is known that tin ions in the plating solution change to metallic tin, which may cause an electrodeposition on the roll surface. This electrodeposited metallic tin also causes defective products such as pressing flaw, and such tendency becomes remarkable when the above-described conventional roll is used.

[0014] It would thus be helpful to provide a cermet powder that enables preparation of a cermet coating having both high wear resistance and high corrosion resistance against a strong acid having a pH of less than 1. It would also be helpful to provide a protective-coating-coated member and an electroplating-bath-immersed roll that are compatible with high wear resistance and high corrosion resistance against a strong acid having a pH of less than 1, as well as their production methods.

(Solution to Problem)

[0015] We thus provide:

(1) A cermet powder containing: tungsten carbide particles in an amount of 40 mass% or more; molybdenum carbide particles in an amount of 10 mass% to 40 mass%; and Ni or a Ni alloy as a matrix metal, wherein the cermet powder further contains chromium, either as a carbide or a metal or alloy element contained in the matrix metal, in an amount of 8 mass% or more.

(2) The cermet powder according to (1) above, wherein the tungsten carbide particles have a content of 70 mass% or less.

(3) The cermet powder according to (1) or (2) above, wherein the tungsten carbide particles have a particle size distribution within a range of 0.1 μm to 6 μm.

(4) The cermet powder according to any one of (1) to (3) above, wherein the molybdenum carbide particles have a particle size distribution within a range of 0.1 μm to 6 μm.

(5) A protective-coating-coated member comprising: a stainless steel base member; and a cermet coating formed on the stainless steel base member, wherein the cermet coating comprises a matrix made of Ni or a Ni alloy, in which tungsten carbide particles and molybdenum carbide particles are dispersed, and, the cermet coating contains the tungsten carbide particles in an amount of 40 mass% or more, the molybdenum carbide particles in an amount of 10 mass% to 40 mass%, and chromium, either as a carbide or a metal or alloy element contained in the matrix, in an amount of 8 mass% or more.

(6) The protective-coating-coated member according to (5) above, wherein the tungsten carbide particles have a content of 70 mass% or less.

(7) The protective-coating-coated member according to (5) or (6) above, wherein the tungsten carbide particles in the cermet coating have a particle size distribution within a range of 0.1 μm to 6 μm.

(8) The protective-coating-coated member according to any one of (5) to (7) above, wherein the molybdenum carbide particles in the cermet coating have a particle size distribution within a range of 0.1 μm to 6 μm.

(9) The protective-coating-coated member according to any one of (5) to (8) above, wherein the cermet coating has a surface roughness Ra of 0.5 μm to 10 μm.

(10) A method of producing a protective-coating-coated member, comprising thermal spraying the cermet powder as recited in any one of (1) to (4) above onto a stainless steel base member.

(11) The method of producing a protective-coating-coated member according to (10) above, wherein the thermal spraying is HVOF thermal spraying.

(12) An electroplating-bath-immersed roll comprising the protective-coating-coated member as recited in any one of (5) to (9) above.

(13) An electroplating-bath-immersed roll comprising a roll shaft portion and a roll body portion, both made of stainless steel, wherein only the roll body portion comprises the protective-coating-coated member as recited in any one of (5) to (9) above.

(14) A method of producing an electroplating-bath-immersed roll, the method comprising: preparing a roll member comprising a roll shaft portion and a roll body portion, both made of stainless steel; and forming a cermet coating only onto the roll body portion by thermal spraying the cermet powder as recited in any one of (1) to (4) above.

(15) The method of producing an electroplating-bath-immersed roll according to (14) above, wherein the thermal spraying is HVOF thermal spraying.

(Advantageous Effect)

[0016] With the cermet powder of the present disclosure, it is possible to prepare a cermet coating that offers both high wear resistance and high corrosion resistance against a strong acid having a pH of less than 1.
Further, the protective-coating-coated member and the electroplating-bath-immersed roll of the present disclosure can achieve both high wear resistance and high corrosion resistance against a strong acid having a pH of less than 1.

BRIEF DESCRIPTION OF THE DRAWING

[0017] In the accompanying drawings:

FIG. 1 is a schematic cross-sectional view of a protective-coating-coated member 100 according to one of the embodiments of the present disclosure; and

FIG. 2A is a schematic cross-sectional view of a conventional electroplating-bath-immersed roll 200, while FIG. 2B is a schematic cross-sectional view of an electroplating-bath-immersed roll 300 according to one of the embodiments of the present disclosure.

DETAILED DESCRIPTION

(Cermet powder)

[0018] A cermet powder according to one of the embodiments of the present disclosure contains: tungsten carbide particles in an amount of 40 mass% or more; molybdenum carbide particles in an amount of 10 mass% to 40 mass%; Ni or a Ni alloy as a matrix metal; and chromium either as a carbide or a metal or alloy element in the matrix, in an amount of 8 mass% or more. With this cermet powder, it is possible to produce a cermet coating that offers both high wear resistance and high corrosion resistance against a strong acid having a pH of less than 1. Each component of the cermet powder of the present disclosure will be described below.

[0019] The tungsten carbide particles serve to impart high wear resistance and relatively high corrosion resistance to the cermet coating. The tungsten carbide particles include for example WC particles. The content of the tungsten carbide particles needs to be 40 mass% or more. The reason is that if it is less than 40 mass%, the cermet coating cannot provide sufficient wear resistance. Also, the content of the tungsten carbide particles is preferably 70 mass% or less. The reason is that if it exceeds 70 mass%, the content of the other components becomes so small that the cermet coating cannot provide high corrosion resistance against a strong acid having a pH of less than 1. From the viewpoint of reliably achieving the effect of the present disclosure, the tungsten carbide particles preferably have a particle size distribution within a range of 0.1 μm to 6 μm.

[0020] The molybdenum carbide particles are important components in the present disclosure, which plays a role of imparting to the cermet coating not only high wear resistance but also high corrosion resistance to a strong acid having a pH of less than 1. The molybdenum carbide particles include for example Mo_2C particles. The content of the molybdenum carbide particles needs to be 10 mass% to 40 mass%. The reason is that if the content is less than 10 mass%, the cermet coating cannot provide high corrosion resistance against a strong acid having a pH of less than 1, and if it exceeds 40 mass%, the content of the other components, in particular, tungsten carbide particles, must be reduced, resulting in insufficient wear resistance of the cermet coating. From the viewpoint of reliably achieving the effect of the present disclosure, the molybdenum carbide particles preferably have a particle size distribution within a range of of 0.1 μm to 6 μm.

[0021] The cermet powder of the present disclosure contains Ni or a Ni alloy as a matrix metal. Examples of the Ni alloy include a NiCr-based alloy, a NiCrMo-based alloy, and a NiCoCrAlY-based alloy, containing Ni as a main component. Ni as a matrix metal plays a role of imparting to the cermet coating high corrosion resistance to a strong acid having a pH of less than 1. From this viewpoint, the Ni content in the cermet powder is preferably 5 mass% or more. Further, in view of the preferable content of the other components, the Ni content in the cermet powder is preferably 20 mass% or less.

[0022] The cermet powder of the present disclosure contains chromium, either as a carbide or a metal or alloy element contained in the matrix metal, in an amount of 8 mass% or more. This chromium plays a role of imparting to the cermet coating high corrosion resistance to a strong acid having a pH of less than 1, and from that viewpoint its content needs to be 8 mass% or more. In view of the preferable content of the other components, the content of chromium in the cermet powder is preferably 20 mass% or less. In the case where the cermet powder of the present disclosure contains chromium carbide particles (Cr_3C_2 particles), from the viewpoint of ensuring the effect of the present disclosure, the particle size distribution thereof is preferably within a range of 0.1 μm to 6 μm.

[0023] The cermet powder of the present disclosure preferably consists of the above components and inevitable impurities.

[0024] In the cermet powder of the present disclosure, the molybdenum content is preferably not less than the chromium content from the viewpoint of imparting to the cermet coating high corrosion resistance to a strong acid having a pH of less than 1.

[0025] Regarding the cermet powder of the present disclosure, its production method is not particularly limited, and it can be produced by a known or arbitrary method such as a melt pulverization method, a sintering pulverization method, or a granulation sintering method.

[0026] (Protective-coating-coated Member and Method of Producing the Same, and Electroplating-bath-immersed Roll and Method of Producing the Same)

Referring to FIG. 1, a protective-coating-coated member 100 according to one of the embodiments of the present disclosure comprises: a stainless steel base member 10; and a cermet coating 20 formed on the stainless steel base member. The cermet coating 20 is formed by thermal spraying the cermet powder of the present disclosure as the thermal spray material onto the stainless steel base member 10. Consequently, in the cermet coating 20, carbide particles 24 containing tungsten carbide particles and molybdenum carbide particles, and optionally chromium carbide, are dispersed in a matrix 22 made of Ni or a Ni alloy. The content and particle size distribution of the tungsten carbide particles, the content and particle size distribution of the molybdenum carbide particles, the Ni content, the chromium content, and the particle size distribution of the chromium carbide particles in the cermet coating 20 are the same as those described above in conjunction with the cermet powder 20. In addition, an electroplating-bath-immersed roll according to an embodiment of the present disclosure comprises the protective-coating-coated member 100. The protective-coating-coated member and the electroplating-bath-immersed roll thus formed according to the present disclosure can achieve both high wear resistance and high corrosion resistance against a strong acid having a pH of less than 1.

[0027] In particular, in the present embodiment, referring to FIG. 2B, it is preferable that a roll member comprising a roll shaft portion 30 and a roll body portion 32, both made of stainless steel, is prepared, and a cermet coating 34 is formed only onto the roll body portion by thermal spraying the cermet powder disclosed herein to thereby produce a electroplating-bath-immersed roll 300.

[0028] According to the present disclosure, the protective-coating-coated member of the present disclosure and the method of producing the same, and the electroplating-bath-immersed roll and the method of producing the same were completed based on our discoveries as described below.

[0029] As mentioned above, using conventional rolls, the life of the rolls and the product yield are greatly reduced in a strong-acid plating bath such as a methanesulfonic acid solution with pH < 1. In order to elucidate this phenomenon and examine countermeasures, our attention was focused on the electrochemical reaction occurring in a roll in the plating solution. First, it was considered that in a conductor roll in a plating bath, unlike ordinary corrosion reaction, a substitution reaction is in progress that is composed of two main reactions, one being a corrosion reaction (anode reaction) in which Fe (or, for example, Ni in the coated layer) becomes ions in the surface and dissolves in the solution, and the other in which Sn ions in the solution undergo electrodeposition (cathode reaction). For example, when the roll component is Fe and the plating component is Sn, these reactions can be expressed as:

cathode reaction:

$$Sn^{2+} + 2e^- \rightarrow Sn \qquad (1)$$

anode reaction:

$$Fe \rightarrow Fe^{2+} + 2e^- \qquad (2).$$

[0030] The reactions of formulas (1) and (2) are electrochemically equivalent, and the total amount of electrons (e^-) generated in the anode reaction is equal to the total amount of electrons consumed in the cathode reaction. On the surface of the conductor roll under such an electrochemical reaction environment, the dissolution reaction proceeds at a portion where the potential increases locally (i.e., anode), while the electrodeposition reaction proceeds at a portion where the potential lowers locally (i.e., cathode).

[0031] In the case where the corrosion potential when the roll is immersed in the solution is relatively high, the sites where these reactions take place can be regarded as being uniformly distributed in microscopic scales, and the corrosion uniformly proceeds over the entire surface. Consequently, the surface morphology can maintain an initial good state. However, under such conditions that the plating solution is a strong acid with pH < 1 or the current density of plating is set excessively high, the reaction may proceed as a result of a cathode or anode reaction taking place in a locally fixed site. In such a case, the surface morphology changes greatly as described below, which may damage the plated product.

[0032] First, with respect to the deposition of plating components such as Sn resulting from the cathode reaction, the reaction tends to concentrate at the site where deposition is initially generated, causing a metal to grow. Then, the grown metal deposit grows to a certain size, then falls off due to a load of, for example, rubbing against the steel sheet, and the site where the cathode reaction concentrates shifts to another place. By repeating such a reaction, deposition of a plating metal such as Sn progresses non-uniformly on the surface, and at the same time fragments of the plating metal that fall off may damage the surface of the steel sheet as a product.

[0033] Further, when the reaction concentrates as a result of the anode reaction being fixed at a certain site, a particular element (such as Fe in the roll) constituting the site is selectively dissolved at the grain boundary or the like, which may cause the roll surface or the coated layer to partially fall off as fragments. These fragments that have fallen off from the surface may damage the surface of the steel sheet as a product.

[0034] In other words, in a conventional roll as described above, the corrosion potential relatively decreases in a strong acid plating bath with pH < 1 or when the current density is excessively high, and the microscopic uniformity of the distribution of the anode and the cathode is reduced, adhesion/detachment of the plating metal and partial damage in the roll surface become conspicuous as a result of localized immobilization, and this may be the cause of decrease in the product yield.

[0035] Therefore, in order to secure the roll life and to maintain a high product yield even in a strong acid plating bath with pH < 1 or even when the current density is set high for the purpose of increasing the line speed, it is necessary to find out a material that can prevent as much as possible the phenomenon in which the reaction would concentrate as a result of a cathode or anode reaction taking place in a locally-fixed site as described above, rather than focusing simply on the amount of reaction. Conversely, providing such a material can prevent the progress of local corrosion as described above, guaranteeing the life of the roll and the product yield.

[0036] In view of the above, static immersion tests were conducted on roll materials in a tin plating solution using methanesulfonic acid with pH < 1, where the change of corrosion potential with time was measured and the degree of substitution reaction was evaluated. The test results revealed that when carbon steel was used as the roll material, the amount of reaction was extremely high, metallic Sn was deposited at every part of the surface, and the deposited lump of metallic Sn repeatedly grew and dropped. On the other hand, when stainless steel such as SUS 316L was used as the roll material, the amount of reaction was considerably low and metal Sn deposition was not found clearly, although a thin reaction layer was observed on the surface. In addition, the reaction layer on the surface could be easily removed by washing with water and chemical washing, and deposition of metallic Sn on the removed surface was not observed. The corrosion potentials at the time when 20 days passed after immersion were compared. As a result, it was found that stainless steel had a potential higher than that of carbon steel by 0.1 V or more, and maintained a potentially noble state.

[0037] From these results, we judged that the amount of reaction is small and immobilization of the anode and the cathode on the surface is not likely to occur even in a strong acid solution with pH < 1 as long as the stainless steel has a corrosion potential of about 0.1 V higher than that of carbon steel. However, since the hardness of stainless steel is at most about HV 200, there is concern that the wear resistance to rubbing against the steel sheet is low. Accordingly, we made further investigations on the material of the coated layer for protecting stainless steel. It is necessary for the material for protecting stainless steel to have high hardness, excellent wear resistance, and good corrosion resistance in a strong acid plating bath. Although carbide cermets are promising as such a material, it is known that good properties cannot be obtained with the ones described in PTLs 1 to 4. However, we determined that these carbide cermets may be able to improve the electrochemical characteristics in a strong acid plating bath by adjusting the components, and engaged in further studies.

[0038] Specifically, samples were prepared by coating the surface of stainless steel as a base member with more than ten kinds of carbide cermet powders for thermal spraying including commercially available ones by HVOF thermal spraying, and immersion experiments were conducted using a strong acid plating solution with $pH < 1.0$. The experimental results revealed that Ni or a NiCr-based alloy is superior for the matrix of the cermet, and when the carbide contains Mo carbide rather than WC particles alone, good corrosion resistance can be obtained. Therefore, as a result of our further investigations, we discovered that in order to obtain high corrosion resistance in a strong acid solution, it is desirable that Cr be contained as carbide or an alloy element in the matrix in an amount of 8 mass% or more and the content of Mo contained as carbide be at least equal to or more than the content of Cr. It was also found that Mo_2C is preferable as the Mo carbide, and that if the content of Mo contained in the cermet is larger than the content of Cr, corrosion resistance will not be impaired, but conversely if the content of Mo is not more than half of the content of Cr, it is difficult to obtain a desired corrosion resistance.

[0039] That is, in a carbide cermet coating for protecting stainless steel from the substitution reaction as described above in a strong acid solution with $pH < 1$ and for ensuring sufficient wear resistance against sliding operation with a steel sheet, it is desirable that carbide particles containing tungsten carbide particles and molybdenum carbide particles are dispersed in a matrix made of Ni or a Ni alloy, wherein the cermet coating contains the tungsten carbide particles in an amount of 40 mass% or more, the molybdenum carbide particles in an amount of 10 mass% to 40 mass%, and chromium either as a carbide or a metal or alloy element contained in the matrix, in an amount of 8 mass% or more. As a matrix containing Ni as a main component, good results were obtained with a NiCr-based alloy, a NiCrMo-based alloy, and a NiCoCrAlY-based alloy.

[0040] Specimens were prepared with a carbide cermet coating satisfying the above conditions being formed on stainless steel by HVOF thermal spraying to form a protective coating, and were subjected to constant-current anode/cathode polarization dissolution experiments. The experimental results demonstrated that the formation of a reaction layer was not significant and the surface morphology was still better than the stainless steel. In addition, as a result of measuring the corrosion potential, a potential higher by about 0.1 V than that of the stainless steel was obtained. The above results indicate that the uniformity of the distribution of the anode and the cathode formed on the surface of the above-described carbide cermet coating formed by HVOF thermal spraying is achieved at a finer level than that of stainless steel. It was thus found that there is almost no possibility of the steel sheet being damaged by the reaction product. In this way, we discovered that a protective layer having good corrosion resistance can be formed even in a strong acid plating bath, while having excellent wear resistance.

[0041] Here, it was determined that it is important to adjust the particle size of the tungsten carbide particles and the molybdenum carbide particles, which are the main components of the cermet, for achieving both wear resistance and corrosion resistance in a trade-off relationship. Specifically, it was found that when carbides, which are the main component of the cermet, having particle sizes of less than 0.1 μm are used, the wear resistance is remarkably deteriorated, and when particles having a particle size of 6 μm or more are used, the uniformity of the distribution of the anode and the cathode in the solution cannot be maintained sufficiently in microscopic scales. It was determined that when the particle size of the tungsten carbide particles and the molybdenum carbide particles is in the range of 0.1 μm to 6 μm, both wear resistance and corrosion resistance can be compatible.

[0042] As a method of forming a protective layer, a high-velocity flame spraying method such as HVOF or HVAF was found to be desirable. For example, when comparing the cermet coating obtained by a high-velocity flame spraying method such as HVOF or HVAF with the cermet coating by plasma spraying or other thermal spraying method, the porosity greatly differs, and in the case of a layer obtained by a thermal spraying method other than the high-velocity flame spraying method such as HVOF or HVAF, it was difficult to maintain a satisfactory surface condition; for example, the solution infiltrated into the layer. Also, when heat treatment is performed on the resulting layer at a high temperature for the purpose of lowering the porosity, the carbide is decarburized into lower carbide or a reaction phase forms with the matrix components, causing a remarkable degradation in wear resistance and corrosion resistance. Such a tendency was also seen in the layers formed by weld overlaying and cladding method. That is, a high-velocity flame spraying method such as HVOF or HVAF is preferable as the method of forming a carbide cermet coating.

[0043] It was found that even with a protective layer formed by a high-velocity flame spraying method such as HVOF or HVAF, the probability of scratching the steel sheet with protrusions of carbide increases when the surface roughness Ra exceeds 10 μm, and when Ra is less than 0.5 μm, the frictional force is not sufficient and the roll idly rotates on the steel sheet, resulting in impairment of the surface condition of the steel sheet. Therefore, the surface roughness Ra of the carbide cermet coating is preferably 0.5 μm to 10 μm.

EXAMPLES

<Example 1>

[0044] Samples were prepared in conformity with conventional roll specifications and roll specifications according to the present disclosure, and subjected to immersion tests for 20 days in a strong-acid plating solution (methanesulfonic acid 50g/L, tin ion concentration 25 g/L) adjusted to pH < 1. Five samples listed in Table 1 were prepared. Specifically, in Sample No. 1, the base member was a conventional carbon steel and the protective layer was also a conventional sample. On the other hand, in Sample Nos. 2 to 5, the base member was made of stainless steel. Regarding the protective layers, Sample No. 2 adopted a conventional layer as in Sample No. 1, and Sample Nos. 3 to 5 used HVOF layers of various carbide cermets using Ni or a Ni base alloy as the matrix; among these, Sample No. 5 corresponds to the cermet specification of our example of the present disclosure. In the layer of Sample No. 5, the Mo content was 9.4 mass%, the Cr content was 8.7 mass%, the WC particle size was 0.1 μm minimum and 6 μm maximum, the particle size of Mo_2C particles was 0.1 μm minimum and 6 μm maximum, and the surface roughness Ra was 3.0 μm. Each sample was prepared such that the exposed portion of the base member and the protective layer portion had substantially the same surface area and devised such that the properties of the boundary portion between the layer and the base member could be evaluated.

[0045] To evaluate the corrosion resistance of the protective layer, the change in mass (weight loss due to corrosion) before and after immersion was measured for each sample, and the results are presented in Table 1. In addition to the change in mass, Table 1 lists the results of observation of the surface conditions of the protective layer with the electron microscope after immersion for 20 days, as well as the measurements of the corrosion potential. Table 1 also lists the results of Suga wear tests (#120-SiC paper, load 3.25 kgf, 400 reciprocations) separately performed on the protective layers. The layer observation results were evaluated according to the following criteria:

Excellent:	almost no change
Good:	slightly changed
Fair:	changed
Poor:	significantly changed

Table 1

Sample No.	Base Member	Coating components	Coating observation results	Corrosion potential (V vs. Ag/AgCl)	Change in mass (g)	Amount of wear (mg)	Category
No.1	SS400	46Ni - 11Cr - 2.5B - 2.5Si - 2.5Fe - 35WC	Poor	-0.7	>0.46	2	Comparative Example
No.2	SUS316L	46Ni - 11Cr - 2.5B - 2.5Si - 2.5Fe - 35WC	Poor	-0.6	0.35	2	Comparative Example
No.3	SUS316L	WC - $20Cr_3C_2$ - 7Ni	Fair	-0.6	0.33	0.5	Comparative Example
No.4	SUS316L	Cr_3C_2 - 60CoNiCrAlY	Fair	-0.5	0.34	1.5	Comparative Example
No.5	SUS316L	WC - $10Mo_2C$ - $10Cr_3C_2$ - 10Ni	Excellent	-0.4	0.26	0.5	Example

[0046] As is clear from the results in Table 1, in the plating solution with pH < 1, the change in mass was significant in Sample Nos. 1 to 4 in accordance with the conventional specifications, particularly in Sample No. 1 using carbon steel as the base member, leading to deterioration in the surface morphology. Furthermore, in the specimens in accordance with the conventional specification using carbon steel as the base member, the boundary between the layer and the base member was markedly broken by corrosion. In contrast, it can be seen that not only the change in mass was small but also the surface morphology was difficult to deteriorate in those samples in which stainless steel was protected with a cermet coating. In particular, in Sample No. 5 which is an example of the present disclosure, the surface morphology was much better than the other samples. This also corresponds to the measurement result of the corrosion potential (the highest in the measurement sample), demonstrating that the uniformity of the distribution of the anode and the cathode on the surface of the coating was excellent. In addition, it can be seen that our examples were excellent also from the viewpoint of wear resistance.

<Example 2>

[0047] Focusing on the mix proportion of the protective layer of Sample No. 5 in Example 1, various cermet powders containing Ni or a Ni-20Cr alloy as a matrix, as well as WC particles, Cr_3C_2 particles, and Mo_2C particles with the adjusted particle size distribution within a range of 0.1 μm to 6 μm, were prepared. Each obtained cermet powder was HVOF thermal sprayed onto a stainless steel to form a protective layer. The composition of the layer in each sample is presented in Table 2. Immersion tests were conducted in the same way as in Example 1, and Suga wear tests were carried out. The evaluation results are presented in Table 2.

Table 2

Sample No.	Chemical composition of coating (mass%)							Evaluation results			Category
								Immersion test		Wear test	
	WC	Cr_3C_2	Mo_2C	Ni	Ni-20Cr	Mo content	Cr content	Coating observation results	Change in mass (g)	Amount of wear (mg)	
1	73	20	0	7	0	0	17.3	Fair	0.33	0.5	Comparative Example
2	75	10	0	15	0	0	8.7	Fair	0.35	0.7	Comparative Example
3	75	10	0	0	15	0	11.7	Fair	0.34	0.7	Comparative Example
4	70	10	10	10	0	9.4	8.7	Good	0.26	0.5	Example
5	70	10	10	0	10	9.4	10.7	Good	0.26	0.5	Example
6	60	10	20	10	0	18.8	8.7	Good	0.25	0.7	Example
7	60	10	20	0	10	18.8	10.7	Good	0.25	0.7	Example
8	50	10	30	10	0	28.2	8.7	Excellent	0.24	0.9	Example
9	50	10	30	0	10	28.2	10.7	Excellent	0.24	0.9	Example
10	50	20	20	10	0	18.8	17.3	Excellent	0.25	1.0	Example
11	40	10	40	10	0	37.6	8.7	Excellent	0.24	1.0	Example
12	30	20	30	20	0	28.2	17.3	Excellent	0.24	1.2	Comparative Example
13	30	20	30	0	20	28.2	21.3	Excellent	0.24	1.2	Comparative Example
14	20	20	50	0	10	47.1	19.3	Excellent	0.23	1.3	Comparative Example
15	10	10	70	10	0	65.9	8.7	Excellent	0.23	1.3	Comparative Example

[0048] As is apparent from the results in Table 2, it is effective to incorporate more Mo_2C particles if it is intended to improve the corrosion resistance to the plating solution, and it is effective to incorporate more WC particles for improving the wear resistance. It is found that Examples 4 to 11 of the present disclosure provided both high wear resistance and high corrosion resistance against a strong acid having a pH of less than 1.

[0049] In each sample in which the cermet powder described in Example 2 was formed into a protective layer by atmospheric plasma spraying method, the porosity was high and the adverse effect such as the deterioration of the carbide was large, and as regards the corrosion resistance and the wear resistance, it was not as good as the layer produced by HVOF thermal spraying.

<Example 3>

[0050] A comparison is made between a conventional product and a product according to the present disclosure when applied to a conductor roll in an electroplating line. FIGS. 2A and 2B illustrate a comparison between the structure of a conventional roll and the structure of a roll according to the present disclosure. In the conventional roll in FIG. 2A, a shaft portion was formed by shrink-fitting a carbon steel tube to a copper shaft core, and a body portion was formed by shrink-fitting a carbon steel sleeve with a protective layer formed thereon by thermal spraying to a roll body portion formed of a carbon steel tube, and these were combined to form a whole roll body. In contrast, in the present disclosure, as illustrated in FIG. 2B, it is only necessary to form a thermal sprayed coating on the roll body made of stainless steel, and it will be readily appreciated that the roll body can be extremely easily fabricated. Sample No. 6 in Example 2 was adopted as the layer specification according to the present disclosure.

[0051] Heat generation by energization of each roll was measured with a thermoviewer, and both were determined to be within the range of 0.14 °C/min to 0.16 °C/min, in which operability is not impaired. The composition of the plating bath was the same as in Example 1. The roll pressing pressure on the steel sheet was 0.2 MPa and the sheet passing speed was in the range of 150 m/min to 490 m/min. Each roll was used for 230 days. After completion of use, each roll was pulled up from the bath, and the surface roughness of the sheet passing portion and the amount of Sn adhesion were investigated. The results are presented in Table 3.

Table 3

	Conventional product	Our product
Ra before use	3.0 μm	3.0 μm
Ra after use	0.81 μm	1.08 μm
Tin adhesion to roll surface	5.2 mass%	4.7 mass%
Failure rate	2.37 %	0.43 %

[0052] The results in Table 3 demonstrated that the surface roughness of the sheet passing portion of each conventional roll decreased from Ra of 3.0 μm before use to Ra of 0.81 μm, which is nearly 1/4, whereas in each roll to which the present disclosure was applied Ra of 1.0 μm or more was maintained after use, and improvement of the layer life of 30 % or more was achieved compared to the conventional ones. It can also be seen that the amount of Sn adhesion was reduced by about 10 % in each roll of the present disclosure as compared with the conventional ones. Both of these results indicate that the corrosion resistance to the plating solution and the wear resistance against the steel sheet can be improved in accordance with the specifications of the present disclosure. In fact, the failure rate of the product was successfully lowered to 0.43 %, which is 1/5 or less, in the case of using rolls of the present disclosure, while it was as high as 2.37 % in the case of using conventional rolls. The reason is considered to be that due to the improvement of corrosion resistance, the damage in the layer which would be the cause of defect and the occurrence rate of coarsen fragments of the electrodeposited Sn were greatly reduced.

[0053] From the results of the same actual operation, it is also found that the use limit of rolls was up to Ra of 0.5 μm in surface roughness, and that the frequency at which the product suffers scratches increased with a roll having an initial surface roughness Ra exceeding 10 μm. Therefore, the surface roughness Ra of the cermet coating according to the present disclosure is preferably from 0.5 μm to 10 μm.

INDUSTRIAL APPLICABILITY

[0054] The cermet powder of the present disclosure can be suitably used as the material of a protective layer (cermet coating) in a protective-coating-coated member such as an electroplating-bath-immersed roll. The electroplating-bath-immersed roll of the present disclosure can be suitably used, for example, as a conductor roll or the like even in an electroplating bath of a strong acid having a pH of less than 1.

REFERENCE SIGNS LIST

[0055]

100	protective-coating-coated member
10	base member (stainless steel)
20	cermet coating
22	matrix
24	carbide particles (WC particles, Mo_2C particles, and optionally Cr_3C_2 particles)
300	electroplating-bath-immersed roll
30	roll shaft portion
32	roll body portion
34	cermet coating (thermal sprayed coating)

Claims

1. A cermet powder containing:

   tungsten carbide particles in an amount of 40 mass% or more;
   molybdenum carbide particles in an amount of 10 mass% to 40 mass%; and
   Ni or a Ni alloy as a matrix metal, wherein
   the cermet powder further contains chromium, either as a carbide or a metal or alloy element contained in the matrix metal, in an amount of 8 mass% or more.

2. The cermet powder according to claim 1, wherein the tungsten carbide particles have a content of 70 mass% or less.

3. The cermet powder according to claim 1 or 2, wherein the tungsten carbide particles have a particle size distribution within a range of 0.1 μm to 6 μm.

4. The cermet powder according to any one of claims 1 to 3, wherein the molybdenum carbide particles have a particle size distribution within a range of 0.1 μm to 6 μm.

5. A protective-coating-coated member comprising:

   a stainless steel base member; and
   a cermet coating formed on the stainless steel base member, wherein
   the cermet coating comprises a matrix made of Ni or a Ni alloy, in which tungsten carbide particles and molybdenum carbide particles are dispersed, and
   the cermet coating contains the tungsten carbide particles in an amount of 40 mass% or more, the molybdenum carbide particles in an amount of 10 mass% to 40 mass%, and chromium, either as a carbide or a metal or alloy element contained in the matrix, in an amount of 8 mass% or more.

6. The protective-coating-coated member according to claim 5, wherein the tungsten carbide particles have a content of 70 mass% or less.

7. The protective-coating-coated member according to claim 5 or 6, wherein the tungsten carbide particles in the cermet coating have a particle size distribution within a range of 0.1 μm to 6 μm.

8. The protective-coating-coated member according to any one of claims 5 to 7, wherein the molybdenum carbide particles in the cermet coating have a particle size distribution within a range of 0.1 μm to 6 μm.

9. The protective-coating-coated member according to any one of claims 5 to 8, wherein the cermet coating has a surface roughness Ra of 0.5 μm to 10 μm.

10. A method of producing a protective-coating-coated member, comprising thermal spraying the cermet powder as

recited in any one of claims 1 to 4 onto a stainless steel base member.

11. The method of producing a protective-coating-coated member according to claim 10, wherein the thermal spraying is HVOF thermal spraying.

12. An electroplating-bath-immersed roll comprising the protective-coating-coated member as recited in any one of claims 5 to 9.

13. An electroplating-bath-immersed roll comprising a roll shaft portion and a roll body portion, both made of stainless steel, wherein
only the roll body portion comprises the protective-coating-coated member as recited in any one of claims 5 to 9.

14. A method of producing an electroplating-bath-immersed roll, the method comprising:

preparing a roll member comprising a roll shaft portion and a roll body portion, both made of stainless steel; and
forming a cermet coating only onto the roll body portion by thermal spraying the cermet powder as recited in any one of claims 1 to 4.

15. The method of producing an electroplating-bath-immersed roll according to claim 14, wherein the thermal spraying is HVOF thermal spraying.

FIG. 1

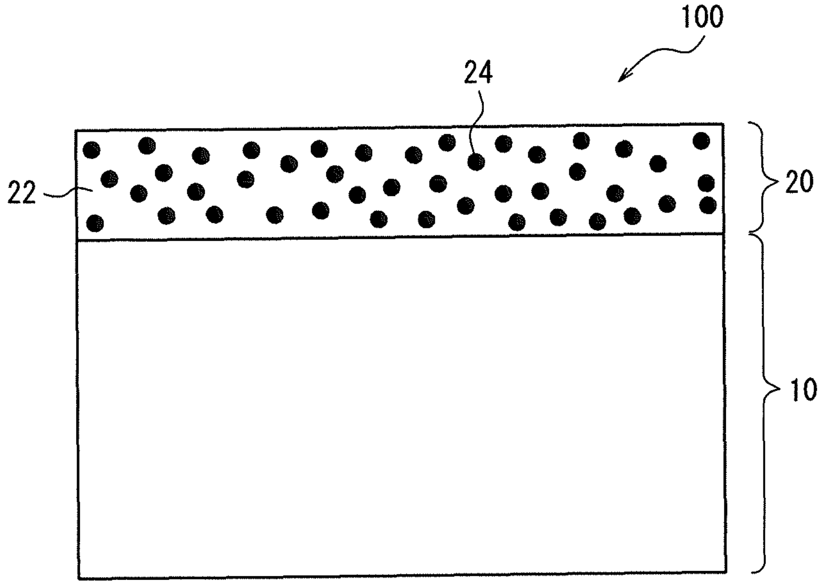


FIG. 2A

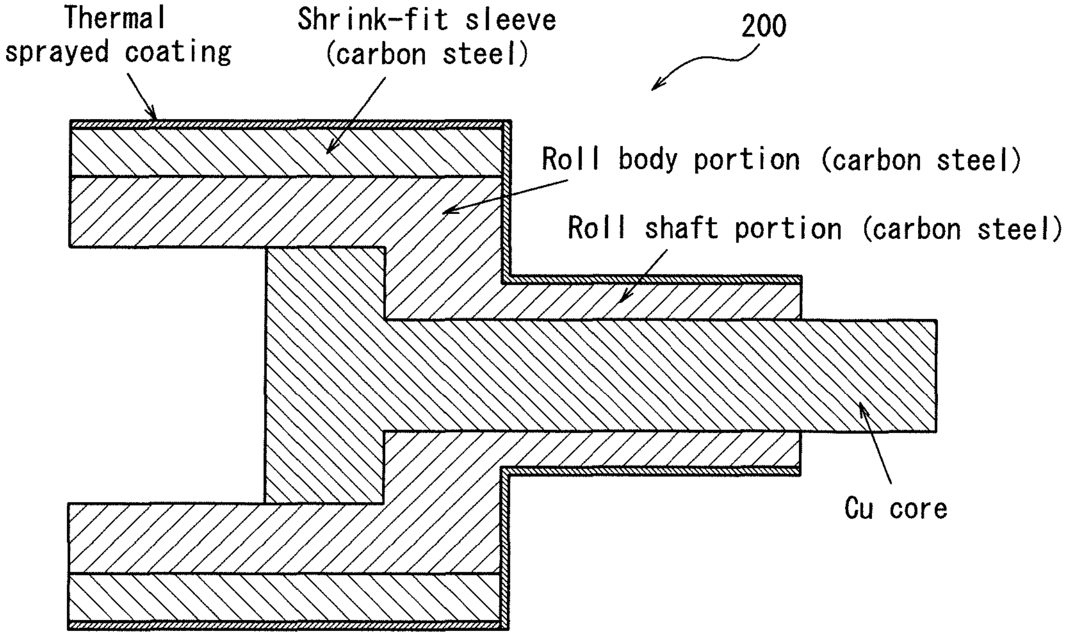
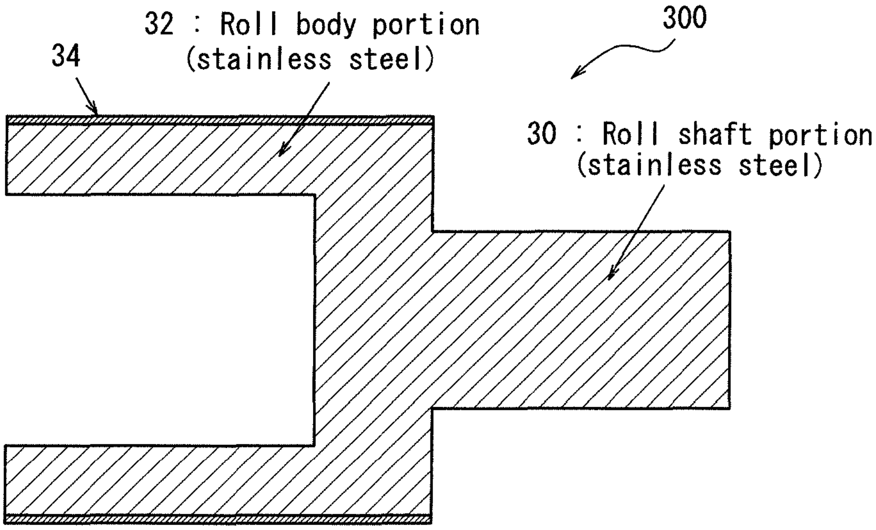

Thermal sprayed coating
Shrink-fit sleeve (carbon steel)
200
Roll body portion (carbon steel)
Roll shaft portion (carbon steel)
Cu core

FIG. 2B


32 : Roll body portion (stainless steel)
34
300
30 : Roll shaft portion (stainless steel)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2017/005385

A. CLASSIFICATION OF SUBJECT MATTER
C23C4/06(2016.01)i, *C22C29/08*(2006.01)i, *C23C4/10*(2016.01)i, *C25D7/06*(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)
C23C4/06, C22C29/08, C23C4/10, C25D7/06

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	1996-2017
Kokai Jitsuyo Shinan Koho	1971-2017	Toroku Jitsuyo Shinan Koho	1994-2017

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.
A	JP 8-311630 A (Sumitomo Metal Mining Co., Ltd.), 26 November 1996 (26.11.1996), claims; paragraphs [0002] to [0006]; example 4 (Family: none)	1-15
A	JP 2006-183107 A (JFE Steel Corp.), 13 July 2006 (13.07.2006), claims; examples (Family: none)	1-15

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

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

Date of the actual completion of the international search
13 April 2017 (13.04.17)

Date of mailing of the international search report
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Name and mailing address of the ISA/
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3-4-3,Kasumigaseki,Chiyoda-ku,
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Authorized officer

Telephone No.

Form PCT/ISA/210 (second sheet) (January 2015)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2017/005385

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 2014-193487 A (Praxair S.T. Technology, Inc.), 09 October 2014 (09.10.2014), claims 1, 4 & US 2007/0261767 A1 claims 1, 4 & WO 2007/133536 A2 & EP 2021524 A2 & CN 101443472 A & RU 2008148951 A & MX 2008014246 A & BR PI0710663 A	1-15
A	WO 2009/060868 A1 (Asahi Glass Co., Ltd.), 14 May 2009 (14.05.2009), claims 1, 5 & KR 10-2010-0085965 A & CN 101848876 A & TW 200932689 A	1-15
A	JP 2002-88461 A (Kawasaki Steel Corp.), 27 March 2002 (27.03.2002), claims; paragraph [0002] (Family: none)	1-15

Form PCT/ISA/210 (continuation of second sheet) (January 2015)

REFERENCES CITED IN THE DESCRIPTION

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- JP 200288461 A **[0004] [0006]**
- JP 2006183107 A **[0005] [0006]**